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Fatty acids: The

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FATS AND OILS

A SERIES OF MONOGRAPHS

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Fatty Acids

Their Chemistry, Properties, Production, and Uses

Second Completely Revised and Augmented Edition

Edited by Klare S. Markley

FATS AND OILS

**A SERIES OF MONOGRAPHS ON THE CHEMISTRY AND
TECHNOLOGY OF FATS, OILS, AND RELATED PRODUCTS**

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FATTY ACIDS

*Their Chemistry, Properties,
Production, and Uses*

**Second Completely Revised
and Augmented Edition**

Edited by

KLARE S. MARKLEY

PART 1

1960

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Fatty acids: The..

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PREFACE TO THE SECOND EDITION

This second edition of *Fatty Acids* follows the general outline and format of the first edition, but is considerably broader with respect to the subject matter covered, and the treatment of prior subjects is more comprehensive than was that of the earlier edition. This broader treatment has been necessitated, in part, by the marked advances that have occurred in this field since the publication of the first edition in 1947.

Considerable expansion of the present work resulted from the more comprehensive treatment of the lower members of the fatty acid series, the hydroxy-, keto-, branched-chain, and polycarboxylic acids and their derivatives. The industrial production and utilization of fatty acids, which were treated only superficially in the first edition, are stressed throughout the present work and also are the subjects of specific chapters.

With few exceptions the present work represents a complete rewriting and not merely a revision of the former edition. To some extent this has resulted from the development of certain specializations in the field which have made it impossible for a single author to treat all phases of the subject with equal degrees of adequacy. In order to provide the reader with the information he desires and needs, a number of outstanding specialists in various fields were invited to participate in the preparation of the present edition. This device introduces certain difficulties, such as variations in style, unevenness of emphasis, breadth of treatment, duplication of subject matter, and other problems. It has been the policy in the present work to allow the individual authors a maximum of freedom in preparing their respective contributions and to defer to the technical editor the responsibility of bringing the completed work into a unified treatise of maximum value to the prospective reader. The result has been, what is believed to be, the most comprehensive work devoted to this subject and is entirely in keeping with the other monographs of this series.

The editor of the present volumes on the chemistry, properties, production, and uses of fatty acids acknowledges the great debt he owes to the contributing authors, without whose assistance such a comprehensive work could not have been prepared. He also wishes to acknowledge the assistance of a number of individuals in preparing his own contributions.

Foremost among these is Mrs. Evald L. Skau who verified and often contributed to the hundreds of references which have been cited. He is also greatly indebted to Mrs. Lygia Bastos de Lemos for the difficult task of typing the numerous tables accompanying the text, and to Miss Yolanda de Castro Sampaio for typing the final draft of this author's manuscripts.

All of the authors of the present work join in thanking the editors of the many journals and the authors and publishers of various books for permission to reproduce certain illustrations; and also those firms and organizations which generously supplied illustrations, data, and technical information for these volumes.

KLARE S. MARKLEY

Rio de Janeiro, Brazil
January, 1960

Publisher's Note

The second edition of *Fatty Acids* was planned originally to contain two parts; the vastness of the subject, however, and the extensive illustrative material make it desirable to extend the size to several volumes. To facilitate using this comprehensive work, the pagination is consecutive from the first to the last volume. Although the last volume contains a cumulative subject and author index for the entire edition, each separate volume contains its own table of contents, list of contributors, and subject index.

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CHAPTER 1

HISTORICAL AND GENERAL

KLARE S. MARKLEY

Rio de Janeiro, Brazil

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1. Introduction

The group of compounds referred to as *fatty acids* were designated thus because they were originally found to be constituents of animal and vegetable fats and fatty oils. The term was originally applied principally to the saturated monobasic carboxylic acids and especially to the long-chain acids, although Chevreul isolated such short-chain acids as butyric as early as 1814 and valeric, caproic, and impure oleic acid between 1818 and 1823 (1). As our knowledge of the natural fats increased, polyunsaturated acids, hydroxy, keto, and branched-chain acids were also found as constituents of these substances, and even acids containing alicyclic substituents.

The term fatty acids has come to be applied more broadly and loosely to include the saturated and unsaturated monobasic carboxylic acids and several series of substituted acids having carbon skeletons identical with the normal saturated acids.

The number of unsaturated and substituted acids found to date in natural fats is limited by comparison with the number of normal saturated acids, but the various series have been extended by synthesis or isolation

from nonfat natural sources (waxes, essential oils, fruit essences, fossiliferous materials, etc.). Other representatives have been found as products of destructive distillation, pulping wood, oxidation of petroleum, and as by-products of processing various natural products. They have also been found as constituents of the phosphatides, sterol and vitamin esters, and other lipid materials which are present in natural fats or which accompany them as produced by modern methods of processing.

Moreover, the fatty acids per se and the substances of which they are natural components undergo spontaneously certain reactions (oxidation, scission, polymerization, etc.) to produce other acids such as aldehydic, keto, and dibasic acids.

Because of these and other considerations, any exposition of the fatty acids must be broader in scope than that encompassed within the original concept of this group of compounds, but the question arises as to where the line should be drawn between the included and the excluded. The answer can probably never be entirely satisfactory to either the author or reader; hence the material selected and treated herein must be considered merely as a compromise devised by the authors and editor to make this exposition as broad as possible and yet remain within the limitation of the allotted space.

The present work, like its predecessor edition, is concerned primarily with the fatty acids and their derivatives rather than with the fats, waxes, fruit essences, essential oils, and other products of which they are components. Nevertheless, reference is made to these substances wherever this has seemed to be desirable or pertinent.

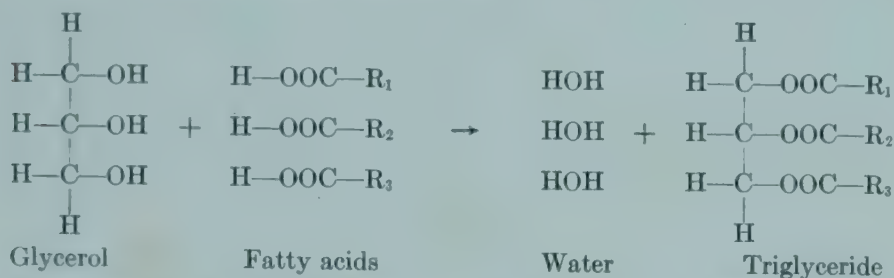
2. Definitions

(a) *Fats and Oils*

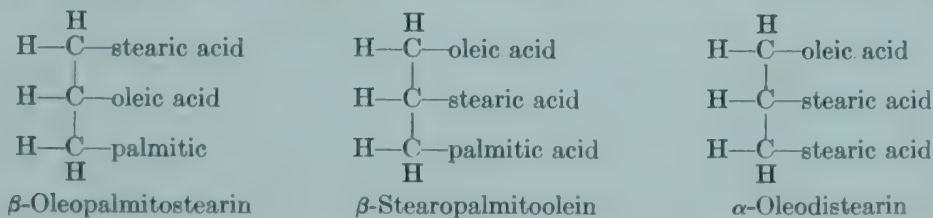
The words *fats* and *oils* have been applied with so many different meanings that it is necessary to define them to avoid misunderstanding in the present usage. As commercial products *fats* and *oils* refer to that class of lipid materials consisting of the glyceride esters of the fatty acids and their associated phosphatides, alcohols, hydrocarbons, pigments, etc., which are obtained from plants or animals by such processes as cooking with water or steam, pressing, extraction with organic solvents, or any combination thereof.

Except for minor quantities of associated or accompanying lipids, some of which are removed by refining, fats and oils consist of triglycerides or

esters of fatty acids formed by the reaction between glycerol and three molecules of fatty acids, as shown below.



In the equation R_1 , R_2 , and R_3 may be the same or different fatty acid radicals. The large number and the complexity of the natural fats and oils have their origins in two sources, namely, the number, kind, and mode of arrangement of the individual fatty acids which are attached to the glycerol skeleton to form specific glycerides, and in the number and relative proportions of such glycerides which are mixed or mutually dissolved to form the specific fat or oil. For example, a natural fat or oil might be composed of the following three triglycerides in different proportions.



In contrast to the natural product, a synthetic one consisting of a single triglyceride containing only one kind of fatty acid residue may also be considered to be a fat or oil. This is also true of a pure triglyceride containing two or even three different fatty acid residues attached to the same glycerol skeleton. Thus a simple triglyceride such as tristearin, oleodipalmitin, or oleopalmitostearin may be considered as a fat or oil.

Whether any one of the foregoing triglycerides or mixture of triglycerides, natural or synthetic, may be referred to as a fat or oil depends on its physical state, that is, whether it is a solid or a liquid, because of the common practice of referring to a solidified oil as a fat and to a liquified fat as an oil. This usage has little scientific foundation because many of the more familiar fats are in reality plastic solids or at least semisolids, consisting at ordinary temperatures of a liquid in intimate admixture with many very small, often microcrystalline, solid particles. At 70°F . (21°C .), for example, only about one-third of the glycerides of natural lard are in the solid state. However, at a sufficiently low temperature any

liquid oil will become completely solidified and at a sufficiently elevated temperature any fat will become a liquid oil. The difference between a fat and oil may, therefore, be considered merely as a difference in physical state which is reversible by altering the temperature in the proper degree and in the required direction.

Changes in state can be effected by means other than a change in temperature. By means of hydrogenation a liquid oil at ambient temperature can be changed into a plastic (semisolid) fat or a completely solid fat at the same temperature. Naturally liquid (α -form) tung or oiticica oil can be converted into a solid fat (β -form) by the action of a trace of iodine or sulfur. These transformations of state are, however, not reversible, and each of the products, either original or transformed, will still exhibit changes of state (liquid $\rightleftharpoons$ solid) with the appropriate change in temperature.

In view of the foregoing, the term *fat* is now quite generally used to include both *fats and oils* where specification of the physical state is of no importance and where the repetitious use of the phrase *fats and oils* becomes monotonous.

(b) *Essential Oils and Fruit Essences*

The essential or ethereal oils differ in composition and properties from the glyceride oils. They are odoriferous substances of an oily nature obtained largely from vegetable sources; generally liquids, but may be semisolid or solid at ordinary temperatures. They are often thought, erroneously, to consist largely of esters of fatty acids. Most essential oils are composed of terpenes, oxygenated constituents, sesquiterpenes, and a small amount of nonvolatile residue; of these the terpenes and sesquiterpenes are most characteristic. The oxygenated compounds include alcohols, aldehydes, ketones, esters, phenols, phenolic ethers, acids, lactones, oxides, coumarins, etc.

The distillation waters of essential oils contain small quantities of fatty acids, especially lower fatty acids, such as formic, acetic, propionic, butyric, and valeric. Most probably they do not occur as such in the oils but are formed by hydrolysis of esters in the course of distillation. Only a few essential oils consist largely of some ester, such as methyl salicylate (wintergreen and sweet birch oils) or linalyl acetate (bergamot, lavender, petitgrain, and clary oils). Orris root oil consists chiefly of myristic acid (83–96%) which accounts for the consistency of the oil but contributes nothing to the odor. Oil of ambrette seed consists principally of pal-

mitic acid but it likewise contributes nothing to the odor of the oil.

Fatty acid esters are often found as constituents of fruit essences, for example, isoamyl isovalerate in bananas; and a large number of simple esters are used in formulating artificial fruit flavors, for example, ethyl and isoamyl butyrates, which are used in making artificial essences of pineapple, banana, strawberry, raspberry, red-currant and peach. Such esters are usually formed by the reaction of short-chain fatty acids.

(c) *Waxes*

The term wax was originally applied to the secretion of the glands on the underside of the abdomen of the worker bee of the genus *Apis*. The bee uses the material to construct its so-called honeycombs. Beeswax appears to be the first substance of this type with which man became familiar; it was clearly different from fats by being harder, more stable, and possessed of a high luster, especially when applied in thin layers and rubbed vigorously. Eventually, other substances having the same or similar properties were discovered and these too were called waxes in analogy to beeswax.

When these substances were subjected to chemical analysis they were found to consist essentially of esters of long-chain monohydric alcohols and monobasic acids admixed with various amounts of the same or similar long-chain alcohols and acids in unesterified form, hydrocarbons, sterols, resins, and other minor constituents. Waxes, therefore, came to be defined as esters of long-chain monohydric alcohols and long-chain fatty acids, but with the passage of time the word assumed a broader significance and came to be applied to various substances, natural and synthetic, which had little or nothing in common with true waxes, except such physical attributes as hardness, luster, chemical stability, etc. Solids such as paraffin hydrocarbons, long-chain alcohols, acids and esters of dihydric alcohols, which were hard and lustrous and which had a waxy feel and appearance, were referred to as waxes, especially in trade literature.

Moreover, various oily (sperm and jojoba oils) and greasy (wool grease) substances, which in nowise resembled beeswax or other hard waxes, were found to consist essentially of esters of monohydric alcohols and monobasic fatty acids. Some waxes (Japan waxes) were also found to consist essentially of esters of dibasic acids, but despite the general broadening of the term, the majority of the natural plant and insect waxes still conform to the original chemical distinction between fats and waxes.

3. History

Man has been familiar with fats since prehistoric time. Long before he had any knowledge of the chemical nature of these substances he recognized differences in their properties and employed them in a variety of ways. The use of fats as foods was probably instinctive but other applications no doubt resulted from observations of the properties and behavior of these substances under various environmental conditions. When and how man first became familiar with these substances and their manifold uses is lost in antiquity, but certainly fats, as well as waxes, were employed by primitive peoples of all climes as medicinals, in cosmetics, in religious ceremonies, as illuminants and lubricants, and for other purposes.

The ancient Egyptians and Phoenicians used vegetable oils for food and for anointing their bodies, but not for illumination. From them, knowledge of the application of fats and oils spread to the Hebrews, and thence to the Greeks.

Friedel (2) analyzed the contents of a number of earthen vases found in the interior of Egyptian tombs believed to predate the First Dynasty (ca. 3200 B.C.). One of these vases contained several kilograms of a pale brown, porous, granular substance which was found to consist of palmitic acid mixed with less than 51% of tripalmitin, indicating that the original material was a palm oil that had undergone oxidation and partial saponification. Another vase contained a firmer, more granular, paler mass consisting of stearic acid with about 30% tristearin and was probably beef or mutton tallow. A third vase, containing material similar to the first-mentioned, contained palmitic acid and 41% tripalmitin. These materials were probably intended as provisions for the dead. Other smaller vases contained unidentifiable fatty material mixed with galena which was probably used as a cosmetic.

Klemgard (3) mentions the fact that the Egyptians used olive oil as a lubricant for moving large stones, statues, and building materials and that axle greases consisting of a fat and lime together with other materials were used in lubricating Egyptian chariots as early as 1400 B.C.

Sarton's (4) *Introduction to the History of Science* contains many references to the use of fats and oils in the arts, technology, and medicine from the dawn of Greek and Hebrew knowledge (9th to the 8th centuries B.C.) to the Middle Ages. The Homeric poems contain a reference to the use of oil in weaving. Candles, made of beeswax and tallow, were known to the Romans and probably were used by others in pre-Roman times.

According to Davidsohn, Better, and Davidsohn (5), soap was made by the Phoenicians as early as 600 B.C.; they used it as an article of barter with the Gauls. These authors state that it is not known whether the Romans learned the use of soap from the ancient Mediterranean peoples or from the Celtic inhabitants of Britannia who produced soap from fats and plant ashes and gave the product the name "saipo" from which the word soap is derived.

Soap, both as a medicinal and as a cleansing agent, was known to Pliny (23–79 A.D.) who mentions both hard and soft soap, and it may be inferred that soaps were known considerably prior to Pliny's time. According to Pliny, soap appears to have been made by boiling goat's tallow with causticized wood ashes to produce a soft soap which was converted to hard soap by repeatedly treating the pasty mass with salt or sea water. Excavations of Pompeii, which was destroyed in 79 A.D., has revealed at least two buildings equipped as soap factories.

The Greek physician Galen (ca. 130–200 A.D.) mentions soap as a medicant and body-cleansing agent and the physician Theodorus Priscianus (ca. 385 A.D.) mentions it as a shampooing agent. Geber (Jabir ibn Hayyan), the famed Arab chemist who lived about 800 A.D., repeatedly mentions soap in his writings.

Waxes, as well as resins, were used as protection against moisture, especially in shipbuilding and in some forms of wall painting. An early form of painting known as *encaustic*, actual specimens of which are known in the form of portraits on late Egyptian mummy cases and which was certainly used before then on wall decorations, employed a mixture of pigments in natural waxes. Another early form of painting known as *tempera* employed an emulsion of wax or oil, water, pigments, and an emulsifying agent such as a vegetable gum or egg yolk.

Varnishes were certainly used in Egypt on mummy cases of the New Empire. Many of these varnishes are insoluble, but their method of preparation is not known with certainty. The earliest mention of the use of a drying oil in a process connected with painting is given by Aetius about the 6th century A.D., who stated that nut oils dry and form a protective varnish. From this time on, the use of drying oils and varnishes seems to be well established and recipes dating from the 8th or 9th century A.D. are known for transparent varnishes composed of linseed oil and natural resins.

Theophilus Presbyter, an unknown craftsman, who lived about the end of the 11th and the beginning of the 12th century, devoted many chapters of his *Diversarum artium schedula* to the preparation and use of oil colors.

Theophilus used linseed oil together with some kind of resin, probably amber, copal, or sandarac. He gives many recipes for the preparation of paints, varnishes, and dyes. However, the discovery of the effect of driers in linseed oil paints, which is accredited to the brothers van Eyck, was not made until the first half of the 15th century.

The extensibility of oil upon the surface of water appears to have been known by Greek sailors and was applied by them to subduing waves during a storm. This phenomenon of surface tension or extension of oil upon the surface of water, was investigated by the great Hindu mathematician Bhāskara who is presumed to have lived about 1114 to 1178 A.D.

The American Indian apparently was long familiar with many oil-producing plants and employed them as food, medicine, cosmetics, and illuminants. Standley and Steyermark (6) state that the Indians of Panama strung the oil-rich nuts of a species of *Virola* on thin splinters of wood and used them as candles. In Belém, Brazil, the author was told that the natives of the Amazon followed a similar practice with the nuts of *Virola surinamensis* and *V. sebifera* (ucuhuba nuts). Elsewhere in South America the nuts of various species of oilpalms appear to have been similarly used.

✓ As animal and vegetable fats were used from the time of the earliest records, methods for their separation must have been devised before the dawn of history. Probably the first fats used by man were of animal origin—tallows and greases—which were separated from other tissue simply by heating or boiling with water. Certain oily fruits, for example, the olive and the African oilpalm in the Old World and the avocado in the New, as well as certain oil-rich nuts may likewise have been made to yield their oils in the same manner. In the oilpalm (*Elaeis guineensis*) belt of west Central Africa, as well as in Brazil, the natives still produce oil by boiling the fruit of the oilpalm with water after preliminary fermentation and maceration of the pulp. Long before the advent of Europeans in the Western Hemisphere, the natives in many parts of South and Central America produced oils from various palm and other oil-rich nuts by crushing the kernels, roasting the crushed mass, and boiling it with water. This process is still practiced in isolated parts of South America and was observed by the author (7) in the interior of the State of Bolivar, Venezuela, south of Caicara, where it was being applied to the kernels of the coroba palm (*Scheelea macrolepis*).

Recovery of oil from small seeds with extremely hard seed coats required the development of more vigorous methods of processing and probably gave rise to cooking, grinding, and pressing processes. However,

these too are of very ancient origin. Cotton was manufactured and cottonseed crushed for oil and cake by the Hindus as early as the 5th century B.C. and possibly earlier. Old medical books of the Hindus recommended cottonseed oil for external applications and described the method of extracting it by pounding the seed and then boiling it with water. It is believed that about this same time cottonseed oil was produced in China by grinding in edge runner mills followed by heating and pressing in wedge presses.

The Hebrews possessed oil mills powered by treads that were usually operated by prisoners. According to Blank (8), sesame, linseed and castor oils were produced in Egypt by pressing as early as 259 B.C., and that as early as 184 B.C. screw and wedge presses, filters, and edge runner mills were used in Rome for the production of oil.

Pliny the Elder (23–79 A.D.) described olive, rice, almond, sesame, grapeseed, walnut, and palm oils. He also described an olive oil mill which resembled the edge runner, the stones being flat on the inner side and convex on the outer side. The Greeks and Romans are said to have employed screw presses similar to wine presses for recovering olive oil.

The wedge press was used in very early times in the Orient, particularly in China, where it is still operated. Another type of extractor, known as ghani, chekku, or kolhu, was developed long ago in India. It operates on the principle of a pestle rotating in a mortar and is often powered by bullocks. The ghani is still used in remote areas of India (9).

Ample evidence exists to attest the fact that the peoples of all early civilizations were acquainted with a variety of fats and waxes, various methods for producing them, and a considerable number of uses and applications. Aside from their use as food, they were used in the manufacture of protective and decorative coatings, soaps, and cosmetics, as illuminants, medicinals, lubricants, and in religious ceremonies. The primary applications of these substances are very much the same today as those which prevailed in antiquity. However, in addition to the uses prevailing since remote times they are now employed in numerous ways unknown to the ancients.

The uses of fats and oils which were known prior to the beginning of the 19th century were based on empirical knowledge that had accumulated slowly over many centuries, whereas many of the present-day uses have stemmed largely from a knowledge of the composition, structure, properties, and reactions of these substances, and of their component fatty acids and derivatives, obtained through the application of scientific methods of research.

A number of important discoveries concerning the chemical nature of fats were made almost at the birth of modern organic chemistry. Scheele obtained glycerol by heating olive oil with litharge in 1779 and in 1813 Chevreul began his researches on fats which culminated in the classical work, *Recherches chimiques sur les corps gras d'origine animale*. In 1814 he isolated butyric acid from butter; in 1816 established the glyceride nature of fats; in 1817 he prepared stearic acid; and between 1818 and 1823, valeric, caproic, and impure oleic acid.

In 1819 Poutet converted oleic acid to elaidic acid by treatment of the former with the oxides of nitrogen, but the acid was not isolated until 1832 by Boudet. In 1828 Gussierow differentiated oleic and other unsaturated acids from palmitic and stearic on the basis of the differential solubility of the lead salts of these acids. A year later Lefèvre observed that tallow could be treated with sulfuric acid to yield fatty acids. In 1834 Runge prepared the first "sulfonated" oil by the action of sulfuric acid on olive oil; in 1841 Varrentrapp observed that the fusion of oleic acid with caustic soda gave palmitic and acetic acids; in 1844 Pelouze and Gélis synthesized tributyrin by the direct esterification of glycerol and butyric acid; and in 1849 Darby isolated erucic acid. Only the classical study of esterification by M. Bertholet between 1853 and 1862 can be compared with Chevreul's contribution to the chemistry of fatty acids.

Among Bertholet's contributions was the demonstration in 1854 of the trihydric nature of glycerol, the synthesis of the first non-glycerol polyhydric alcohol esters in 1855, the synthesis of mono-, di-, and triglycerides, and the suggestion that natural fats consisted of mixtures of heteroglycerides rather than mixtures of homoglycerides.

During the remainder of the century little progress was made in the fundamental chemistry of fats and fatty acids, but many useful analytical tests were developed and many practical developments occurred which were to continue at an accelerated pace during the first half of the 20th century. New and more efficient methods of saponification were introduced, as well as the vacuum-distillation of fatty acids and glycerol and the solvent extraction of fats; Turkey red oil was prepared by sulfonation of castor oil (1875); margarine and linoleum were invented and commercial manufacture of these products was begun in various countries.

Various factors appear to have retarded the chemists' interest in natural fats during the second half of the 19th century. Foremost of these, no doubt, was man's long familiarity with these products, and the fact that over a period of centuries a considerable empirical knowledge concerning them had been acquired, permitting the establishment of numerous

industries devoted to the processing of these products for consumption as food, in soapmaking, and in the manufacture of paints, varnishes, and related products. Generally, there were no burdensome surpluses of fats and oils and they did not accumulate as by-products in the manufacture of other products, as was the case with coal tar; hence they presented no disposal problem and they were not a source of cheap raw material.

From the academic point of view, fats were not attractive research materials as they were not readily crystallizable and few crystalline derivatives could be prepared from them. Furthermore, they were considered to be very simple substances or, at best, more or less complex mixtures of triglycerides of fatty acids. They were assumed to possess few characteristic chemical or physical properties, and they could not be separated into definite chemical entities by any simple method such as crystallization or distillation.

The process of saponification by means of which fats can be broken down to produce fatty acids has been known for about twenty centuries, but the mixtures of fatty acids produced by saponification apparently were no more attractive to the organic chemist than were the original natural fats. Here again, simplicity of structure of the individual acids, the difficulty of isolating them in pure form and, in the case of the unsaturated acids, the difficulty of converting them to crystalline derivatives appear to have been among the chief reasons for their neglect. The fatty acids were known to consist of a relatively long, saturated or unsaturated, hydrocarbon chain with a terminal carboxyl group. It was assumed that such simplicity of structure afforded little opportunity for applying newly discovered ingenious reactions which were being applied so effectively in other directions in preparing hitherto unknown organic compounds. During this period of development of classical organic reactions, hydrocarbon chemistry, based on petroleum, was in its infancy, and the chemistry of high molecular weight polymers was unknown. However, the development of numerous products from petroleum hydrocarbons, followed by the application of polymerization reactions to many simple organic molecules, undoubtedly stimulated the chemist to turn to the natural fats and their derived fatty acids as a source of raw materials for the production of similar products.

Nevertheless as late as 1924, Armstrong (10) in a Presidential address entitled, *A Neglected Chapter in Chemistry*, presented at the annual meeting of the Society of Chemical Industry, stated: "This account of our knowledge of the fats and of some of the many problems needing study, particularly in the organic branch of chemistry, is mainly written with the

hope of reviving interest in them as, apart from physical and analytical investigations, *no other province of chemistry has been so little studied in recent years.*"

Strangely enough, about this time a renaissance in the chemistry of fats had its inception, and the tempo of research in this field began to increase at an accelerating rate. The increased interest in the chemistry of fats and fatty acids became evident not only in the expansion and diversification of the literature on the subject, but also in the appearance of scientific journals devoted solely to publication of research in this field. Bull (11) has referred to the fact that, in 1932, *Chemical Abstracts* contained approximately 800 abstracts on various phases of lipid chemistry compared to approximately 150 in 1917, and according to Deuel (12), *Chemical Abstracts* for 1947 contained approximately the same number as in 1932, indicating that activity in this field has continued to be relatively high.

It is difficult to pinpoint the causes for the rapid expansion of interest in fat chemistry that began to be evident in the late 1920's. One of these seemed to have stemmed from the application in 1902 by W. Normann of Sabatier and Senderens's discoveries in hydrogenation to the hardening of liquid oils. This reaction gave a new impetus to investigations into the chemical behavior of fats and produced an extensive literature on the subject.

It is little noted or remarked upon today that two men, perhaps more than any others, were responsible for awakening a worldwide interest in the chemistry of fats. Prof. T. P. Hilditch of the University of Liverpool and Dr. George S. Jamieson of the U. S. Department of Agriculture, not only carried out and published a very large number of researches on fats and fatty acids, but they gave the English-speaking world a series of books and monographs which brought together and systematized the rapidly accumulating knowledge in this field. They investigated many heretofore little known fats and clarified many problems concerning the composition and constitution of these as well as the better known ones; they contributed new techniques of analysis and improved old ones; and above all they trained many young men who in their turn have made numerous and valuable contributions to our knowledge of these substances.

Hilditch (13) brought out the first edition of his *Industrial Fats and Waxes* in 1927 and Jamieson (14) his *Vegetable Fats and Oils* in 1932; followed by Hilditch's (15) *Chemical Constitution of Natural Fats* in 1940. These monographs were the forerunners of many English language monographs devoted to the general subject of fats and fatty acids or to some specialized field or allied branch thereof. Hilditch and Jamieson had

their counterparts in Germany and other countries; their influence was appreciable but they did not create the impact of these two.

The first quarter of the 20th century also saw the founding of new scientific societies and journals devoted to the interests of scientists specializing in the chemistry and technology of fats, oils, and derived and allied products. These were followed in the next quarter with the founding of special laboratories and institutes in various parts of the world which were devoted largely or exclusively to research on fats and fatty products.

The new investigators who were attracted to the field were not content to continue to analyze fats in terms of their fatty acid and glyceride composition and characterize them by a limited number of physical properties that often did not distinguish one fat from another. New tools and techniques were introduced and investigations were directed toward the crystallographic, thermal, dielectric, electromagnetic, absorption, radiation, and solution properties of fats and fatty acids.

These investigations led to the discovery of heretofore unknown substituted and isomeric acids, some of which had been suspected to occur in natural or processed fats but could not be detected or identified.

Biochemical and specially nutritional investigations multiplied and diversified in many directions. Many classical organic synthetic reactions were applied to fats and fatty acids, which led to the discovery of new commercially important products, and simultaneously dispelled the idea of the simplicity and lack of reactivity of these substances. It was found that these substances were capable of undergoing many types of reactions including condensation, polymerization, isomerization, oxidation and reduction, many types of esterification, interesterification, addition and substitution reactions, etc.; in other words they exhibited many reactions that were considered the classical reactions of organic chemistry.

4. Sources

Various lipids, including the glyceride esters or fats, the glycerophosphoric acid esters or phosphatides, sterol esters, vitamin esters, and related fatty compounds, occur in almost every type of plant and animal cell and often represent a large part of the total constituents of specialized organs such as seeds, nuts, tubers, animal livers, intermuscular connective tissue, the abdominal cavity, and subcutaneous connective tissue. Hence, whenever any plant or animal material is extracted with certain organic solvents, such as diethyl ether, chloroform, petroleum naphtha, benzene,

TABLE 1

Fats and Oils: Estimated World Production, Averages 1935-39, 1945-49, 1950-54
1955-58, Annual 1959-60^a, in 1,000 Short Tons

Commodity	Average					Fore- cast 1960
	1935-39	1945-49	1950-54	1955-58	1959 ^b	
Edible vegetable oils ^c						
Cottonseed	1,390	1,220	1,693	2,004	2,170	2,250
Peanut	1,665	1,880	1,906	2,239	2,520	2,395
Soybean	1,050	1,530	2,014	2,870	3,685	3,670
Sunflower	625	830	910	1,183	1,595	1,300
Rapeseed	1,330	1,150	1,021	1,208	1,295	1,260
Sesame	715	705	745	655	665	680
Olive Oil	975	917	1,113	1,095	1,125	1,460
<i>Total</i>	7,750	8,232	9,402	11,254	13,055	13,015
Palm oils ^d						
Coconut	2,135	1,620	2,089	2,309	2,000	2,000
Palm kernel	400	335	440	446	465	475
Palm	1,090	1,000	1,279	1,371	1,400	1,410
Babaçu kernel	25	35	37	49	55	60
<i>Total</i>	3,650	2,990	3,845	4,175	3,920	3,945
Industrial oils ^c						
Linseed	1,145	1,100	1,081	1,139	1,110	1,140
Castorseed	200	210	221	228	225	240
Oiticica	10	12	10	14	1	10
Tung	150	118	123	129	135	135
Perilla	65	5	5	4	4	5
<i>Total</i>	1,570	1,445	1,440	1,514	1,475	1,530
Animal fats						
Butter (fat content)	4,190 ^e	3,450 ^f	3,652	3,995	4,100	4,200
Lard	3,485	3,100	3,993	5,123	6,510	6,700
Tallow and greases	1,615	2,018	2,575	3,194	3,630	3,710
<i>Total</i>	9,290	8,568	10,220	12,312	14,240	14,610
Marine oils						
Whale	545	280	439	430	415	440
Sperm whale	30	40	78	116	125	125
Fish (including liver)	480	275	456	514	490	500
<i>Total</i>	1,055	595	973	1,060	1,030	1,065
Estimated world total	23,315	21,830	25,880	30,315	33,720	34,165

^a Beginning with 1950 the years shown refer to the years in which the predominant share of the oil was produced. In former publications of this table the years shown were the years in which the oil-bearing materials were produced and not necessarily when their oils were extracted.

^b Preliminary.

^c Estimates of oil production from oilseeds are based on the assumption that for each of the oilseeds produced a certain proportion—which varies from one oilseed to the next—is crushed for oil.

carbon tetrachloride, acetone, and the like, there is obtained a soluble product generally containing a fat or oil as the principal constituent. Such extractions are made as a matter of course in every proximate analysis of plant or animal tissue but few of these extracts have been examined with respect to their composition and properties. Probably each separate plant or animal organ extracted in this manner yields a fat different in composition from any other fat. In the majority of cases the differences are only of a minor nature, while in others unusual constituents may be present, as has been shown by the investigation of a number of fats elaborated by certain pathogenic microorganisms. Investigations in recent years have established the existence in nature of an appreciable number of fats containing fatty acids having branched aliphatic chains, cyclic substituents, triple bonds, keto groups, and various systems of conjugated double bonds. What other unique structures remain to be discovered cannot be surmised.

Probably less than a thousand fats from all sources have been examined even superficially. Many of these are of academic interest only and many others are of interest primarily because of their biological rather than economic significance. The known fats and oils of economic or industrial significance probably do not exceed a few hundred. Hilditch (15) described in his first edition of the *Chemical Constitution of Natural Fats* 420 fats from plant species, about 80 from land animals, and about 100 of aquatic origin. In some instances these numbers included fats from different parts of the same plant or animal. Since the appearance of Hilditch's monograph in 1940 the number and diversity of known plant fats have increased appreciably, as may be seen by reference to Eckey's (16) recent (1954) comprehensive book on this subject.

According to a report of the U. S. Department of Agriculture (17), the estimated world production of fats and oils in 1959 was about 33.7 million short tons divided as shown in Table 1. Of the 33.7 million tons of fats, approximately 15.3 million tons were derived from land and marine animals and 18.4 million tons from plant sources. Actually the total production was probably considerably larger because this figure does not include a relatively large number of minor oils which are produced and consumed

^a Estimated on the basis of exports and the limited information available on production and consumption in the various producing areas.

^b 1934-38 average.

^c 1946-49 average.

Source: U. S. Department of Agriculture, Foreign Agricultural Service, *Foreign Crops and Markets*, January 23, 1958, and January 28, 1960.

locally in many countries and which generally do not appear in world statistics. For example, Paraguay annually produces about 4000 tons of mbocayá palm kernel and pulp oils (18); Brazil produces about 7000–8000 tons of tucum, murumurú, patuá, curuá, macaúba, licuri, pracaxi, andiroba, and other oils from indigenous plants (19); El Salvador produces about 500 tons of aceituna kernel oil (20); Mexico and Guatemala process the kernels from a number of different American oil palms and other indigenous plants (21); and similar production might be cited for almost every country of Latin America, and no doubt for other countries as well.

In addition to the oils mentioned in Table 1 there is a considerable production of other oils from the germs of various cereal grains (corn, sorghum, wheat, rye, etc.); of so-called vegetable butters (cocoa, ucuhuba, mowrah, etc.). The list of minor oils might be multiplied appreciably, but it would have only a qualitative significance because there is no practical means for estimating their total contribution to the world's production and consumption of these products. It has been stated that these oils may equal about 10% of the total world consumption. It is, however, reasonably certain that of the total annual *in situ* production of oils by wild palms and other wild oil-bearing plants, only a very small part is commercially exploited, usually because for one reason or another it is uneconomical to do so.

In addition to plants, animals contribute to the world's supply of fatty materials large amounts of fats in the form of butter, lard, tallow, greases, and marine oils. The total of this contribution is considerably larger than indicated by the figures in Table 1 because there is much production of such fats, especially from land animals, on the farm, in the home, and for local consumption which never enter into trade channels or official statistics.

There are also other sources of fats and fatty acids, some of which are produced on a relatively large scale. These include tall oil (22), a by-product of pulping wood; greases recovered by rendering garbage and offal animals; by-product acids from the destructive distillation of wood and other organic materials; volatile and nonvolatile acids produced by fermentation or other action of microorganisms on sugars, starches, etc.; and synthetic acids from hydrocarbons and other intermediates.

5. Fatty Acid Industry

Although still closely allied with the fat and oil industry, the production and utilization of fatty acids has grown in magnitude and diversity to a

TABLE 2. Total Fatty Acids: U.S. Supply, Disposition, and Utilization, 1943 to 1959 (Almond Counts)

I. HISTORICAL AND GENERAL

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Utilization in nonfood products

Drying oil products

Year	Supply			Disposition		Drying oil products							
	Production ^b	Im-ports	Stocks Jan. 1 ^c	Total	Ex-ports	Domestic disappearance	Other						
							Soap ^b	Paint and varnish ^b	Lino-leum and oil-cloth ^b	Resins	Other	Total	Other
1943	516	4	53	573	7	502	181	7	1	3	d	11	310
1944	541	2	64	607	5	547	208	12	2	2	d	16	323
1945	588	2	55	645	4	590	254	14	2	3	d	19	317
1946	621	1	51	673	3	611	233	15	1	4	d	20	358
1947	474	1	59	534	27	465	98	12	2	8	d	22	345
1948	425	1	42	468	25	403	68	11	2	5	d	18	317
1949	498	2	40	540	53	429	56	12	2	5	d	19	354
1950	651	3	58	712	60	584	77	15	4	11	d	30	477
1951	595	3	68	666	50	536	78	17	3	9	1	30	428
1952	548	4	80	632	40	517	61	28	3	12	2	45	411
1953	512	3	75	590	24	491	60	34	1	23	5	63	368
1954	500	1	75	578	15	487	64	30	1	23	4	58	365
1955	517	1	56 ^b	572	17	498	70	37	..	33	13	83	345
1956	545	1	56 ^b	602	27	514	62	23	1	28	10	62	390
1957	505	1	61	567	23	483	59	22	d	28	10	60	364
1958	462	1	61	521	47	423	55	20	d	21	10	51	303
1959	681	1	68	750	28	641	e	e	e	e	e	e	e

^a Totals computed from unrounded data.^b Prior to 1949, includes fatty acids derived from tall oil.^c Prior to 1950, includes only fatty acids from fractionating stearic, oleic, and solid fatty acids.^d Less than 500,000 pounds.^e Data not available as of April 1, 1960.

Source: *Oilseeds, Fats and Oils, and Their Products 1909-1953*, U. S. Department of Agriculture Statistical Bulletin No. 147, Washington, June 1954. Later data and revisions of earlier data provided by the Agricultural Marketing Service, U. S. Department of Agriculture.

TABLE 2a

U.S. Factory Consumption of Specified Animal and Vegetable Fatty Acids: United States Totals and Specified End Uses, 1956
(Thousand Pounds)

Item and year	Total	Stearic acid (40-50% stearic content)	Other stearic acids (high palmitic and hydro- genated animal vegetable fatty acids)	Fish and marine mammal fatty acids	Coconut-type fatty acids	Oleic acid including white oleic and red oil	Unsaturated fatty acids			Low rosin fatty acids ^a
							Animal	Veg- etable	unhydrogenated fatty acids	
Total Factory Consumption	414,138	50,902	54,540	8,322	59,950	59,948	91,266	69,984		19,226
Processing ^b	92,934	608	1,862	(D)	1,665	2,472	78,100	8,175		(D)
Edible products	2,995	(D)	(D)	...	(D)	...	...	(D)		...
Chemicals, including metallic soaps and driers	58,728	11,576	10,709	2,283	4,339	16,856	866	10,727		1,372
Lubricating and similar oils, total ^c	24,607	3,141 ^d	7,280	1,727	91	6,402 ^e	4,710	278		978
Lubricants and greases	19,063	1,667	7,195	1,580	81	3,435	4,596	(D)		(D)
Paint and varnish	22,494	(D)	100	80	1,388	(D)	728	15,115		4,624
Pharmaceuticals	3,780	2,459	301	...	501	(D)	...	(D)		...
Polishing preparations and similar protective coatings	4,131	1,163	(D)	201	(D)	1,623	(D)	284		616
Resins and plastics, including alkyd resins	37,450	1,159	4,477	...	3,804	3,434	...	18,152		6,424

Rubber products and com- pounds	30,040	10,892	13,299	(D)	819	2,129	...	1,324	(D)
Soaps, excluding shampoos and metallic soaps	19,411	3,147	9,035	(D)	8,913	9,792	5,872	9,531	(D)
Synthetic organic deter- gents, including wet- ting agents	42,594	2,459	(D)	2,141	34,144	3,239	(D)	460	123
Textile auxiliaries other than soap, dyes, and wetting agents	10,310	1,826	1,133	213	699	5,794	444	42	159
Toilet articles, including shampoos	6,699	3,609	276	...	499	2,269	(D)	(D)	...
(Other miscellaneous products	27,965 ^c	8,191 ^e	5,878	506 ^b	(D)	5,442 ^d	(D)	5,375	1,967
Not shown separately	...	672	190	1,171	3,088	496	546	521	2,963

... Represents zero.

(D) Withheld to avoid disclosing figures for individual companies.

^a Comparable data available for 1955 but not for 1954 because in the latter year the quantities of low rosin fatty acids consumed were not reported separately but were included in the statistics for refined tall oil.

^b Includes hydrogenation, sulphonation, fat-splitting and pressing.

^c Includes metalworking, core oils, brake fluids, dielectric oils, and cutting oils, as well as lubricants and greases shown separately, when the release of these statistics does not disclose figures for individual companies.

^d Includes 1460 thousand pounds consumed in metalworking.

^e Includes 949 thousand pounds consumed in metalworking and 1724 thousand pounds consumed in cutting oils.

^f Includes quantities (in thousands of pounds) consumed in the following end products: leather, 1091; candles, 2966; animal feeds, 2139; glue, 490; paint and ink vehicles, 800; printing ink, 478; and artists' materials, 3933.

^g Includes 2684 thousand pounds consumed in candles and 229 thousand pounds consumed in artists' materials.

^h Includes 187 thousand pounds consumed in leather.

ⁱ Includes 343 thousand pounds consumed in leather and 315 thousand pounds consumed in printing ink.

Source: U.S. Department of Commerce, *Facts for Industry*, Series M28-1.a-06, June 12, 1957. Data from a one-time survey by the Bureau of Census, not repeated up to April 1, 1963.

point where it can rightly be considered a separate industry. Compared to the fat and oil industry whose origin is lost in antiquity, the fatty acid industry is comparatively recent. Its inception goes back no farther than to the classical researches of Chevreul from 1811 to 1825 on the saponification of fats and the isolation and identification of various fatty acids, including stearic and oleic, and culminating in the issuance of a French patent to Chevreul and Gay-Lussac in 1825 for the separation of fatty acids and their utilization in the manufacture of candles.

These discoveries were soon applied to the production of so-called "stearin" and "red oil," terms applied to crude stearic and oleic acids, respectively. As originally produced these products represented little more than the separation of the mixed fatty acids of saponified inedible tallow into saturated (solid) and unsaturated (liquid) fractions by the method known as "panning and pressing."

The solid or "stearin" fraction, actually a mixture of stearic and palmitic acids in the ratio of about 45 to 55%, soon came into considerable demand for the manufacture of candles which had heretofore been made largely from beeswax and spermaceti. With the availability of stearic acid it became the principal constituent of candles and remained so until the advent of paraffin, first prepared from Scotch shale in 1850, and subsequently from petroleum.

Thereafter "stearin" or commercial stearic acid and paraffin became, and continues to be, the common ingredients used in the manufacture of candles.

The liquid or "red oil" fraction, which is produced simultaneously with the solid stearic acid fraction by "panning and pressing" saponified tallow, in addition contains 65–70% oleic acid, linoleic and saturated acids and unsaponifiable matter in about equal proportions. Uses were also found for this fraction as a textile lubricant, for the manufacture of soaps for various textile applications, for the manufacture of greases, and for the manufacture of sulfonated "red oil."

The original "panning and pressing" method, with many modifications and improvements, is still used extensively, but during the first half of the present century other methods, including distillation and solvent fractionation, were introduced for the separation of fatty acids. In reality neither process was entirely new. Gay-Lussac obtained a patent in 1825 for the separation of fatty acids by distillation, and in 1870 the first patent was issued in the United States for the recovery of glycerol by distillation. In 1882 Armandy produced glycerol by vacuum distillation. However, these processes were not applied on a large industrial scale for

the separation of fatty acids until the present century when industrial demand arose for fatty acids other than stearic and oleic.

To satisfy this demand there appeared on the market cottonseed, soybean, corn, coconut, and palm kernel fatty acids. These products were unfractionated or grossly fractionated mixtures of fatty acids produced by distillation in relatively crude stills. A further demand arose for relatively homogeneous individual fatty acids which in turn led to the development of improved methods of fractional distillation. These processes were applied on an industrial scale with selected stocks to produce the entire series of homologous fatty acids from caproic to stearic.

Thus, during a period of a century and a quarter following the appearance (1823) of Chevreul's classical researches on the saponification of animal fats and the separation of fatty acids and the first crude applications of these discoveries, there has developed an industry involving an investment of millions of dollars in plants and equipment, producing approximately 550,000 thousand pounds of product annually in the United States alone, not to mention those other countries in which counterparts of this industry exist.

The magnitude of the production, the diversity, and the uses of fatty acids may be seen by reference to Tables 2 and 2a.

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CHAPTER II

NOMENCLATURE, CLASSIFICATION, AND DESCRIPTION OF INDIVIDUAL ACIDS

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1. Introduction

The naturally occurring fatty acids may be divided on the basis of the absence or presence of double and triple bonds in their hydrocarbon chains.

into two broad classes termed saturated and unsaturated. The saturated fatty acids, if they contain no branching side chains, are referred to as *normal* alkanolic acids and may bear the prefix *n*-, for example, *n*-caproic or *n*-hexanoic. The unsaturated fatty acids may contain one or more double or triple bonds. If an unsaturated acid contains only double bonds it is termed an alkenolic, ethenolic, or olefinic acid. If it contains only triple bonds it is called an alkynolic, ethynolic, or acetylenic acid.

The unsaturated acids may be further subdivided on the basis of the number of double bonds in the hydrocarbon chain into monoalkenolic (monoethenolic), dialkenolic (diethenolic), etc. The polyalkenolic acids may also be classified as *unconjugated* or *conjugated* depending on the relative positions of the double bonds. If the double bonds are separated by one or more single-bonded carbon atoms, $\text{—C=C—C}_n\text{—C=C—}$, the acid is said to be unconjugated. When double-bonded carbon atoms are adjacent to one another, —C=C—C=C— , the acid is referred to as conjugated.

If one or more hydrogen atoms of the hydrocarbon chain are substituted with some other atom or radical, such as halogen, hydroxy, or keto, the acid may retain its specific name and be prefixed by the name and position of the substituent atom or group, such as 2-chlorobutyric acid, 9,10-dihydroxystearic acid, or 10-methylstearic acid. In a few instances the acid may have a distinctive name as well. Thus, 12-hydroxyoleic acid is known as ricinoleic acid after the plant from which it was first obtained. There are still other classes of acids, such as the alicyclic acids represented by the chaulmoogra series which are more often than not referred to by specific names indicating their plant or animal origin rather than by their systematic names.

Much confusion exists in the older literature with reference to the nomenclature of the specific fatty acids. Once it was common practice to name each new or supposedly new acid by reference to its specific source without accurate knowledge of its structure. To some extent this practice is still followed. These names provide no clue to the structure of the acid and are generally quite meaningless in this respect. Not infrequently, different names have been assigned to the same acid isolated by different workers, or different names have been assigned to different specimens of the same acid of different degrees of purity.

Similar confusion existed in the past with respect to other classes of organic compounds and it was eventually resolved by the development of a scientific or systematic nomenclature. The development of this no-

menclature and its application to the fatty acids is discussed in the next section.

2. Nomenclature

Almost from the dawn of modern organic chemistry the need for a rational system of naming compounds was recognized. By the middle of the 19th century the rapidly expanding number and diversity of known compounds led to the proposal of several systems of nomenclature. Chemical nomenclature has two principal uses, namely, (a) to provide a readily recognizable name that can be used in referring to a given compound in the various forms of communication, and (b) to serve as a means of cataloging or indexing compilations of organic compounds such as Beilstein's *Handbuch* and the numerous abstract journals such as *Chemical Abstracts*.

For the first purpose trivial or common names can serve to a limited extent but these may vary considerably from one language to another. For the second purpose only a scientifically designed and internationally recognized and applicable system can suffice.

As the number of known organic compounds multiplied the need for a systematic nomenclature became more and more acute. Prior to 1892 a number of such systems had been proposed (1) and were applied with various degrees of success. An international congress of chemistry, held in connection with the Paris Exposition in 1889, appointed an International Commission of Chemical Nomenclature which met in Geneva in 1892 and adopted a set of resolutions that became known as the Geneva System (2) of chemical nomenclature. These rules found only partial acceptance and were not complete, but they covered most of the aliphatic compounds including the fatty acids and most of their derivatives.

Clarification and extension of the Geneva System resulted from the adoption by the Council of the International Union of Chemistry in Liege in 1930 of the Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry (3). This report was based on the rules of the Geneva Congress but modified and expanded in certain respects. These rules became known as the Modified Geneva System.

The International Union of Pure and Applied Chemistry, at its 16th meeting in New York in 1951, adopted a number of additional rules and modified in minor respects some of the previous ones. These rules are referred to as the IUPAC-Geneva System.

The last-mentioned system is used by *Chemical Abstracts* but in order to improve its system of indexing it has adopted an order of precedence

of functions and a list of prefixes and suffixes for distinguishing various radicals, groups, and functions in organic compounds.

The confusion in the nomenclature of the fatty acids and their derivatives has gradually given way to a simple and rational system of names but not all of the previous existing difficulties have disappeared. This is due to the fact that trivial names still find considerable usage and because alternatives are permitted under the Geneva and the IUPAC-Geneva systems.

The English system of trivial names arose from the practice of adding the suffix "-ic" to a root indicative of the natural source or some property of the acid, for example, acetic acid from the Latin *acetum*, vinegar; stearic acid from the Greek *stear*, tallow; palmitic acid from palm oil; oleic acid from the Latin *oleum*, oil.

Under the rules of the Geneva System, the aliphatic acids are regarded as derivatives of hydrocarbons of the same number of carbon atoms (CH_3 -being replaced by $-\text{COOH}$). The name of the acid is formed from the name of the hydrocarbon and the suffix "oic." The presently accepted names for the hydrocarbons are given in Table 3. With the appropriate prefixes and suffixes they can be used to name the fatty acids, alcohols, acid halides, etc.

For the normal saturated fatty acids, the final "e" of the corresponding hydrocarbon is changed to "oic." If the saturated acid contains two carboxyl groups the suffix becomes "dioic," and for three carboxyls, "trioic," etc.

Thus, butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, becomes butanoic acid from butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, and the suffix "oic." Palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$, becomes hexadecanoic acid from hexadecane, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$, and the suffix "oic." In a similar manner the monounsaturated (alkenoic) acids are designated by adding "oic" to the Geneva name for the corresponding unsaturated hydrocarbon, thus, the acid $\text{CH}_3\text{CH}:\text{CHCOOH}$ is designated as butenoic acid from butene and the suffix "oic." Oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, is octadecenoic acid from octadecene. Triply bonded acids are similarly designated by dropping the final "e" of the corresponding hydrocarbon and adding the suffix "oic." Thus, tetraric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{C}:\text{C}(\text{CH}_2)_4\text{COOH}$, becomes octadecynoic (formerly octadecinoic) acid from the triple-bond hydrocarbon **Octadecyne** (formerly octadecine) and "oic."

If the unsaturated acid contains a multiple number of double bonds in the hydrocarbon chain, the combining form di-, tri-, tetra-, etc., is inserted before "enoic" to indicate the number of such double bonds. Thus, oleic,

TABLE 3
Nomenclature of the Aliphatic Hydrocarbons

Number of carbon atoms	Alkanes, ^a C_nH_{2n+2}	Alkenes, ^a C_nH_{2n}	Alkynes, ^a C_nH_{2n-2}
1	Methane	—	—
2	Ethane	Ethene	Ethyne ^b
3	Propane	Propene	Propyne ^c
4	Butane	Butene	Butyne
5	Pentane	Pentene ^d	Pentyne
6	Hexane	Hexene	Hexyne
7	Heptane	Heptene	Heptyne
8	Octane	Octene	Octyne
9	Nonane	Nonene	Nonyne
10	Decane	Decene	Decyne
11	Hendecane ^e	Hendecene	Hendecyne
12	Dodecane	Dodecene	Dodecyne
13	Tridecane	Tridecene	Tridecyne
14	Tetradecane	Tetradecene	Tetradecyne
15	Pentadecane	Pentadecene	Pentadecyne
16	Hexadecane ^f	Hexadecene	Hexadecyne
17	Heptadecane	Heptadecene	Heptadecyne
18	Octadecane	Octadecene	Octadecyne
19	Nonadecane	Nonadecene	Nonadecyne
20	Eicosane	Eicosene	Eicosyne
21	Heneicosane	Heneicosene	Heneicosyne
22	Docosane	Docosene	Docosyne
23	Tricosane	Tricosene	Tricosyne
24	Tetracosane	Tetracosene	Tetracosyne
25	Pentacosane	Pentacosene	Pentacosyne
26	Hexacosane	Hexacosene	Hexacosyne
27	Heptacosane	Heptacosene	Heptacosyne
28	Octacosane	Octacosene	Octacosyne
29	Nonacosane	Nonacosene	Nonacosyne
30	Triacontane	Triacontene	Triacontyne
31	Hentriacontane	Hentriacontene	Hentriacontyne
32	Dotriacontane	Dotriacontene	Dotriacontyne
33	Tritriacontane	Tritriacontene	Tritriacontyne
40	Tetracontane	Tetracontene	Tetracontyne
50	Pentacontane	Pentacontene	Pentacontyne
60	Hexacontane	Hexacontene	Hexacontyne
70	Heptacontane	Heptacontene	Heptacontyne

^a Nomenclature approved by the International Union of Chemistry.

^b Formerly ethine, propine, etc.

^c Also called allylene.

^d Also called amylenes.

^e Formerly undecane.

^f Also called cetane and corresponding olefin called cetene.

linoleic, and linolenic acids, containing one, two, and three double bonds, respectively, are designated octadecenoic, octadecadienoic, and octadecatrienoic.

The presence of multiple triple bonds in the hydrocarbon chain is similarly indicated by inserting the same combining forms before "-ynoic." Tariric acid with one triple bond is designated octadecynoic acid. Isanic acid, which has one double bond and two triple bonds in the hydrocarbon chain, is called octadecendiynoic acid.

A modification of this method of nomenclature is the use of a Greek numeral root to indicate the number of carbon atoms in the chain and the generic suffix "-oic" to designate a saturated acid; "-enic" to designate an acid containing one double bond; and "-ynic" to designate an acid containing one triple bond. Under this system stearic, oleic, and stearolic acids would be named octadecoic, octadecenic, and octadecynic, respectively. These designations are little used today but are met with in the older literature.

In order to provide a designation for a specified carbon atom in the hydrocarbon chain at which a substituent may be attached or where unsaturation may occur, the original Geneva System provided a method of numbering the carbon atoms of the aliphatic saturated acids in which the carbon atom of the terminal carboxyl group was numbered 1 and the successive carbon atoms 2, 3, etc. According to this system, the acid corresponding to the formula $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$ would be designated as bromo-2-butanoic acid or 2-bromobutanoic acid, and the acid corresponding to the formula $\text{CH}_3(\text{CH}_2)_7\text{CHOH}(\text{CH}_2)_8\text{COOH}$ would be designated as 10-hydroxyoctadecanoic or 10-hydroxystearic acid. This system of numbering and nomenclature has also been adopted by *Chemical Abstracts* for indexing purposes (4).

The Geneva system also provided for numbering the aliphatic acids on the basis of the carboxyl group (carboxylic system) as a substituent of the corresponding hydrocarbon and, therefore, designates as number 1 the carbon atom adjacent to the terminal carboxyl group (3). In this system, butyric acid becomes 1-propane-carboxylic acid and 2-bromobutanoic acid becomes 1-bromo-1-propane-carboxylic acid. This system corresponds with the long-practiced method of designating the carbon atoms of the hydrocarbon chain of the acids by the Greek letters α , β , γ , etc., beginning with the carbon atom adjacent to the carboxyl as α . Thus, the acid corresponding to the formula $\text{CH}_3\text{CHClCH}_2\text{COOH}$ would be designated as β -chlorobutanoic or β -chlorobutyric acid.

According to the preferred Geneva System (IUPAC-Geneva System)

and that used by *Chemical Abstracts*, the bromobutyric acids corresponding to the formulas $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$, $\text{CH}_3\text{CHBrCH}_2\text{COOH}$, and $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{COOH}$ would be designated 2-bromobutanoic, 3-bromobutanoic, and 4-bromobutanoic acids, respectively. According to the usage of Greek letters they would be designated α -bromobutyric, β -bromobutyric, and γ -bromobutyric acids, respectively.

According to the original Geneva System, the acid corresponding to the formula $\text{CH}_2\text{:CHCH}_2\text{COOH}$ is named butene-1-carboxylic-4, in which the terminal methylene carbon is numbered 1. Under the modified system (3) it would be named 3-butenic or 3-propene-1-carboxylic acid (Rule 64). *Chemical Abstracts* likewise would designate this acid as 3-butenic.

Greek letters were once widely used to designate the positions of carbons or the position of attachment of substituents in the aliphatic acid chain. They are still employed, for example, with the trivial names of acids by *Chemical Abstracts* and in the naming of amino acids, many of which can be considered as substituted aliphatic acids.

The Greek letters ω and Δ have been and sometimes are still used with special significance in naming of fatty acids. Omega is often used to designate the terminal carbon atom farthest removed from the carboxyl, irrespective of the length of chain.

The Greek letter Δ with a superscript numeral or numerals was once widely used to designate the presence and position of one or more double or triple bonds in the hydrocarbon chain of aliphatic acids. Thus, ordinary oleic acid was designated as $\Delta^{9,10}$ -octadecenoic acid, and tariric acid as $\Delta^{6,7}$ -octadecynoic acid. Some authors used only one number to designate the position of a double bond in which case oleic acid would be Δ^9 -octadecenoic acid, as the double bond is assumed in this case to be between the carbon atom designated and the next higher-numbered carbon atom. *Chemical Abstracts* omits the use of the Δ and also uses only one number to designate the position of the double bond. Thus, linoleic acid is simply designated as 9,12-octadecadienoic acid rather than as $\Delta^{9,10,12,13}$ -octadecadienoic acid. The *Chemical Abstracts* usage is simple and unambiguous, and has almost entirely replaced the other more cumbersome systems.

Fatty acids containing one or more double bonds, like other ethylenic compounds, exhibit geometric isomerism, and it is often necessary to distinguish between *cis*- and *trans*-forms. In the case of systematic names this is done by the use of the prefixes *cis*- and *trans*-, but with naturally occurring acids and some synthetic acids with common names, the specific name may be sufficient. For example, oleic and elaidic refer to the *cis*-

and *trans*-forms, respectively, of $\Delta^{9,10}$ -octadecenoic acid. In other common names containing -oleic and -elaidic (or elaido-), the former denotes a *cis* and the latter a *trans* form, thus myristoleic refers to *cis*- $\Delta^{9,10}$ -tetradecenoic acid and petroselaidic to *trans*- $\Delta^{6,7}$ -octadecenoic acid. Isomeric forms arising from the presence of two or more double bonds in fatty acids often need to be distinguished when they are referred to by their systematic names, but generally not when common names are used. Linoleic acid, for example, refers specifically to *cis*-9,10, *cis*-12,13-octadecadienoic and linolelaidic to *trans*-9,10, *trans*-12,13-octadecadienoic acid.

Because of the large number of possible isomers (positional and geometric) of unsaturated acids and the difficulty of isolating and identifying them, there exists considerable confusion in the names of such acids in the literature. Common names have been extended to include other isomers: *trans*-oleic has been used to refer to elaidic acid, and linoleic sometimes denotes any straight-chain unsaturated fatty acid containing 2 double bonds and 18 carbon atoms. The prefix "iso-" has at times been used broadly to refer to any or all isomers of well-known acids, as isooleic acids. Greek letters have been employed to distinguish between certain isomers, for example, α - and β -eleostearic acids.

Branched-chain acids, as phthioic, and substituted fatty acids, as ricinoleic and the chaulmoogra-oil acids, exhibit optical isomerism resulting from the presence of one or more asymmetric carbon atoms. Various systems of naming optically active stereoisomers have been used, including (+)- and (-)- to indicate the direction of rotation, and carbohydrate prefixes such as D-*threo*- and L-*erythro*- and D-*ribo*- and L-*xylo*-, as in naming the stereoisomeric dihydroxystearic acids. The prefixes *cis*- and *trans*- have often been used erroneously to denote such configurations.

It has been common practice in the past to name acyl radicals RCO-, by changing the ending -ic in the trivial names of acids to -yl, as acetyl from acetic acid. Geneva names involve this same change of -ic to -yl (or -oic to -oyl), as decanoyl from decanoic. In some instances the use of the same ending for related acyl and alkyl radicals has lead to ambiguity, e.g., lauryl (lauroyl) to refer to $\text{CH}_3(\text{CH}_2)\text{CO}_{10}$ - as in lauroyl chloride, $\text{CH}_3(\text{CH}_2)_{10}\text{COCl}$.

The Commission on Organic Nomenclature of the International Union of Pure and Applied Chemistry recommended in September, 1949, that the -oyl ending be used to name all carboxylic acid radicals, e.g., stearoyl for $\text{CH}_3(\text{CH}_2)_{16}\text{CO}$ —, except for those derived from formic, acetic, and oxalic acids. The acid radicals derived from the last-named retain their

previous names, formyl ($\text{HCO}-$), acetyl ($\text{CH}_3\text{CO}-$), and oxalyl ($-\text{OCCO}-$).

Then ending *-yl*, except as mentioned above, is reserved for univalent radicals, as stearyl for $\text{CH}_3(\text{CH}_2)_{17}-$. It may be combined with a designation for unsaturation, as in propenyl, $\text{CH}_3\text{CH}:\text{CH}-$, or ethynyl, $\text{CH}:\text{C}-$. The ending *-ylene* denotes a bivalent radical in which (except in the case of methylene, $\text{H}_2\text{C}=\text{}$) the two free valences are on different atoms, as, trimethylene, $-\text{CH}_2\text{CH}_2\text{CH}_2-$. When the two free valences of a bivalent radical are on the same atom the ending used (except for methylene) is *-ylidene*; as ethylidene, $\text{CH}_2\text{CH}=\text{}$. For three free valences on the same atom the ending is *-ylidyne*; as ethylidyne, $\text{CH}_3\text{C}\equiv$.

Although the nomenclature of the fatty acids has become fairly standardized, reference to the older literature and in some cases to relatively recent work reveals a variety of names applied to the same compound. For example, the saturated fatty acid corresponding to the formula $\text{CH}_3(\text{CH}_2)_5\text{COOH}$ may be referred to as *n*-heptanoic, *n*-heptoic, hetylic, enanthic, and oenanthic, and that corresponding to $\text{CH}_3(\text{CH}_2)_7\text{COOH}$ as *n*-nonanoic, *n*-nonoic, nonylic, and pelargonic.

Piper, Chibnall, and Williams (5) examined a number of naturally occurring acids designated as lignoceric, cerotic, montanic, and melissic. In all cases the natural acids were shown to consist of variable mixtures of two or more acids of the same homologous series. They suggested that the use of these names should be discontinued when reference is made to the pure acids corresponding to the formulas $\text{C}_{23}\text{H}_{47}\text{COOH}$, $\text{C}_{25}\text{H}_{51}\text{COOH}$, etc. The trivial names are, however, still used in many instances, but it is generally understood that the systematic name applies to the pure acid and the common or trivial name to the natural product.

Prior to the development of modern methods of purification and identification various odd-numbered carbon acids were reported from natural sources. Margaric (daturic), $\text{C}_{17}\text{H}_{34}\text{O}_2$, was frequently reported from both plant and animal sources. Wehmer (6) lists fourteen plant sources from which this acid was allegedly isolated. These older products are now known to consist of mixtures of palmitic and stearic acids of an approximate mean molecular weight corresponding to *n*-heptadecanoic acid. In recent years a considerable number of authentic odd-numbered carbon atoms have been isolated from natural fats and these are invariably referred to by their systematic names.

3. Alkanoic (Paraffinic) Acids

(a) Normal Alkanoic Acids

The empirical formula for all of the members of the normal saturated fatty acid series is $C_nH_{2n}O_2$ where n may be any even or odd integer. Since all the acids of the series, except formic, consist of an alkyl chain and terminal carboxyl group, they may be conveniently represented by the formula $RCOOH$ and all members above acetic by the formula $CH_3-(CH_2)_nCOOH$. The lower members of the series are liquids at ordinary temperatures, but as the series is ascended the individual members become increasingly more viscous and ultimately pass to crystalline solids. The lower members are soluble in water and exhibit weakly acidic properties compared to the strongly dissociated inorganic acids. As will be discussed more fully elsewhere, the boiling points increase, and the specific gravity decreases with increased molecular weight, whereas the dissociation constant varies only slightly from member to member.

The systematic and trivial names, formulas, formula weights, and various properties of all members of the series formic to octatriacontanoic are given in Table 4.

All of the even-numbered acids from acetic to octatriacontanoic occur either in the free or combined state in nature, and all of them from butyric to octatriacontanoic are present either as glycerides or as monoesters in fats or waxes.

Until very recently only two odd-numbered carbon atom fatty acids had been reported to be constituents of natural fats. These were valeric and margaric. The former was subsequently proved to be an iso acid and the latter a mixture of palmitic and stearic acids. However, in the past decade all of the odd-number acids from pelargonic to nonadecanoic have been reported to be minor components of a number of fats including human hair fat, ox fat, and fish liver oils. It may be expected that an increasing number of such acids will continue to be reported from a greater diversity of sources.

Formic Acid, $HCOOH$. Formic or methanoic acid, lowest member of the series of normal saturated acids, does not occur as a constituent of natural fats but is obtained by pyrolysis of many organic substances. It was first obtained by distillation of the red ant, *Formica rufa*, from which it derives its name. It has been reported to occur in the stinging nettle, pine needles, oil of hops, various fruits, and other plant organs, as well as in muscle and blood, and in caterpillars.

Corrao (6a) reported the results of an investigation of the soluble volatile acids obtained from several samples of fresh olive oil by means of the Reichert-Meissl-Wollny method as modified by Leffmann-Beam-Polenske. The distillate was subjected to analysis by paper chromatography which gave evidence of the presence of formic, acetic, propionic, butyric, valeric, capronic, and caprylic acids. It does not seem likely that the four lowest acids were present in the oils as glycerides.

Formic acid is a volatile liquid which evolves disagreeably pungent fumes and produces superficial blisters on contact with the skin. The commercial product is usually a 90% aqueous solution which is shipped in stainless steel drums or glass carboys. It is completely miscible with water and forms constant boiling mixtures. Its chemical reactions are similar to other lower homologous carboxylic acids and in addition it exhibits certain anomalous reactions and properties because it contains an aldehyde group, CHO.

Formic acid is made commercially by the formate and formamide processes and as a byproduct in the manufacture of pentaerythritol.

Acetic Acid, CH_3COOH . Acetic or ethanoic acid has been demonstrated as a constituent of the triglycerides present in the lipids of *Ascaris lumbricoides* (7). Synthetic fats have been prepared in which the higher fatty acid radicals have been replaced by acetyl to form diacetotriglycerides having unique properties (8). Acetic acid occurs both free and combined in the form of esters of various alcohols in many plants. It is produced by fermentation through the action of microorganisms and has been detected in animal secretions. It is best known in the form of vinegar which is an aqueous solution containing not less than 4 grams of acid per 100 grams of solution.

Acetic acid is a colorless liquid with a pungent odor. The pure acid, referred to as glacial acetic acid, from the icelike appearance of the crystals, is extremely irritating to the skin and will produce blisters if not quickly removed. Solutions of the acid are used as a preservative for pickles, fish, meats, etc. It is a good solvent for many resins, essential and glyceride oils, and is a basic material in the manufacture of cellulose acetate and acetate plastics, acetic anhydride, ester solvents, metallic acetates, pharmaceuticals, etc.

It is manufactured commercially by (a) fermentation of alcohol, (b) distillation of wood, (c) oxidation of acetaldehyde obtained from acetylene or ethyl alcohol, and (d) a variety of miscellaneous methods of minor importance.

TABLE 4
Alkanoic Acids

Systematic name ^a	Common or other name	Formula	Formula weight	M.p., ° C.	B.p., ° C.	d_4^{20}	n_D^{20}	Neutralization value
Methanoic	Formic	HCOOH	46.03	8.4	100.5	1.220	1.3714	1218.96
Ethanoic	Acetic	CH ₃ COOH	60.05	16.6	118.1	1.049	1.3718	934.26
Propanoic	Propionic	C ₂ H ₅ COOH	74.08	-22	141.1	0.992	1.3874	757.36
Butanoic	Butyric	C ₃ H ₇ COOH	88.10	-7.9	163.5	0.959	1.39906	636.79
Pentanoic	Valeric	C ₄ H ₉ COOH	102.13	-34.5	187.0	0.942	1.4086	549.34
Hexanoic	Caproic	C ₅ H ₁₁ COOH	116.15	-3.4	205.8	0.929	1.4170	483.00
Heptanoic	Heptylic ^b	C ₆ H ₁₃ COOH	130.18	-10.5	223.0	0.922	1.4230	430.96
Octanoic	Caprylic ^c	C ₇ H ₁₅ COOH	144.21	16.7	239.7	0.910	1.4280	389.05
Nonanoic	Pelargonic ^d	C ₈ H ₁₇ COOH	158.23	12.5	255.6	0.907	1.4322	354.56
Decanoic	Capric	C ₉ H ₁₉ COOH	172.26	31.6	270.0	0.895 ³⁰	1.4169 ⁷⁰	325.69
Hendecanoic	Undecylic ^e	C ₁₀ H ₂₁ COOH	186.29	29.3	284.0	0.9905 ²⁵	1.420 ²⁷⁰	301.17
Dodecanoic	Lauric	C ₁₁ H ₂₃ COOH	200.31	44.2	298.9	0.883	1.4230 ⁷⁰	280.08
Tridecanoic	Tridecyllic	C ₁₂ H ₂₅ COOH	214.34	41.5	312.4	0.8458 ⁸⁰	1.425 ²⁷⁰	261.75
Tetradecanoic	Myristic	C ₁₃ H ₂₇ COOH	228.36	53.9	326.2	0.858 ⁸⁰	1.427 ³⁷⁰	245.68
Pentadecanoic	Pentadecylic	C ₁₄ H ₂₉ COOH	242.39	52.3	339.1	0.8423 ⁸⁰	1.429 ²⁷⁰	231.46
Hexadecanoic	Palmitic	C ₁₆ H ₃₁ COOH	256.42	63.1	351.5	0.8534 ⁸²	1.430 ⁹⁷⁰	218.80
Heptadecanoic	Margaric ^f	C ₁₆ H ₃₃ COOH	270.44	61.3	363.8	0.853 ⁸⁰	1.4324 ⁷⁰	207.45
Octadecanoic	Stearic	C ₁₇ H ₃₅ COOH	284.47	69.6	376.1	0.847 ^{69.3}	1.433 ⁷⁷⁰	197.23
Nonadecanoic	Nonadecylic	C ₁₈ H ₃₇ COOH	298.49	68.6	299 ¹⁰⁷	0.871 ²⁴	1.451 ²⁵⁵	187.96
Eicosanoic	Arachidic	C ₁₉ H ₃₉ COOH	312.52	75.3	204 ₁	0.8240 ¹⁰⁰	1.4250 ¹⁰⁰	179.52

***n*-Propionic Acid, $\text{CH}_3\text{CH}_2\text{COOH}$.** Propionic (propanoic) acid is an odd-number carbon acid which has been found in milk, butter, cheese, and other milk products. It contributes to the aroma of butter and cheese and is produced in small quantities by various fermentation processes, especially from carbohydrates such as molasses, by several species of propionic acid bacteria. It has been isolated from straight-run gasoline distillate, gas well condensate, and from products derived by the carbonization of coal and wood.

Propionic acid is a water-white liquid with a pungent odor, miscible with water in all proportions, and is soluble in alcohol and ether. It reacts like other short-chain monocarboxylic acids, forming an acid chloride, anhydride, amide, nitrile, salts, and esters.

The acid is made commercially by several synthetic processes starting with *n*-propyl alcohol, ethylene and steam, or natural gas hydrocarbons. It is shipped in aluminum tank cars and in aluminum and stainless-steel drums.

The acid is used to prepare a variety of esters having fruity and floral aromas, plant and animal hormone esters, cellulose esters, ester plasticizers, and various salts having fungicidal properties.

***n*-Butyric Acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$.** Butyric (butanoic) acid is the lowest member of the acetic acid series found in natural fats. It occurs in small proportions (2 to 4%) as a component of the milk fats of various animals. The disagreeable odor of rancid butter is due principally to the presence of free butyric acid resulting from the hydrolysis of the glyceride. It is also a product of bacterial fermentation of sugars and starches. It occurs in the form of monoesters in certain fruit essences, for example, as the hexyl ester in the fruit of *Heracleum giganteum* and as the octyl ester in *Pastinaca sativa*. It has been reported to occur in the free state in muscle, in perspiration, and in the feces of animals.

Butyric acid is a water-white liquid, soluble in water, alcohol, and other organic solvents. Its reactions are characteristic of the other lower members of the acetic acid series. It is prepared commercially by the oxidation of *n*-butyl alcohol and butyraldehyde. It, together with lactic acid, has been produced industrially by the fermentation of molasses. The acid and its anhydride is used in the preparation of esters employed as flavoring materials with fruity odors. Cellulose ester derivatives are used in lacquers and molding plastic compositions. Tributyrin is used as a plasticizer for cellulose derivatives. It is an intermediate in the preparation of various pharmaceuticals.

***n*-Valeric Acid, $\text{CH}_3(\text{CH}_2)_3\text{COOH}$.** Valeric (pentanoic) acid contains

an odd number of carbon atoms and probably does not occur in natural fats. It has been reported to occur free and in the form of esters in many essential oils and some fruit essences, for example, oil of valerian root (9), rue, catnip, lavender, bergamot, spearmint, geranium, hops, cypress, pineapple (10), *Artemisia verlotorum* (11), etc. Later investigations of these oils have generally shown that the acid was isovaleric instead of the normal acid. Valeric acid has been reported (12) to be the main constituent of the excretions of *Ascaris lumbricoides*. It has also been identified as a constituent of pyroligneous acid, petroleum distillates, and raw cracked gasoline, and it is reported to constitute 53% of kaoliang fusel oil.

It has been found as a constituent of the oxidation products of stearic acid, castor oil, and high molecular weight paraffins; as a product of fermentation of calcium lactate, cellulosic and hemicellulosic materials and their hydrolysates (13), and of the bacterial oxidation of cyclohexane (14).

Valeric acid is a colorless liquid with a putrid odor. It is soluble in water to the extent of only 3.7 g./100 g. at 16° C. It is prepared by the action of carbon dioxide and water on olefins, by the reaction of formic acid with butene, and by the electrolytic oxidation of 1-pentanol.

***n*-Caproic Acid, $\text{CH}_3(\text{CH}_2)_4\text{COOH}$.** Caproic (hexanoic) acid occurs as a constituent of milk fats to the extent of about 2% and in small amounts in coconut oil (<1%), various palm and other oils, and in the lipids of *Ascaris lumbricoides*. It was first isolated from butterfat in 1816 by Chevreul. Oxidative rancidification of butter fats through the action of microorganisms converts caproic acid to *n*-propyl ketone which has an unpleasant odor. Caproic acid has a characteristic odor of goats, hence its name, from the Latin *capra*, goat.

Caproic acid is a colorless oily liquid with slight solubility in water (0.968 g./100 g. at 20° C.), but is readily soluble in ethanol and diethyl ether.

The acid is manufactured commercially by the oxidation of *n*-hexyl alcohol and by the hydrolysis of pentyl cyanide (capronitrile) obtained from 1-pentanol. It can be prepared by the malonic ester and the acetoacetic ester syntheses starting with *n*-butyl bromide. It is used in the manufacture of esters (ethyl, amyl, and allyl) for artificial flavors, and for the introduction of hexyl groups, especially in phenols: hexylphenols, hexylresorcinol, etc.

***n*-Heptanoic Acid, $\text{CH}_3(\text{CH}_2)_5\text{COOH}$.** Heptanoic (enanthic, enanthylic, heptylic) acid contains an odd number of carbon atoms and is not

definitely known to occur in natural fats and waxes although it has been reported to occur in floral waxes. It has also been reported to occur in the essential oils of hops, lavender, violet leaf, and calamas. It is produced during oxidative rancidification and other forms of oxidation of fats; and has been found among the pyrolytic products of shark oils, in a petroleum distillate (15), in cracked cottonseed oil and high molecular weight synthetic paraffins, and in appreciable amounts in various fusel oils.

The acid is an oily liquid with a slight tallowy odor, very slightly soluble in water (0.244 g./100 g. at 20° C.) but is readily soluble in ethanol and diethyl ether. It can be prepared by the oxidation of heptanol using various methods and reagents. It possesses fungistatic properties and growth-inhibiting action on microorganisms.

n-Caprylic Acid, $\text{CH}_3(\text{CH}_2)_6\text{COOH}$. Caprylic (octanoic) acid has a fairly wide distribution in both animal and vegetable fats, but it rarely exceeds about 8% of the total fatty acids. It occurs to the extent of 1 to 4% in milk fats, and 6 to 8% in coconut (7 to 8%) and some other palm kernel oils, but it is also found in some seed oils, notably grapefruit, sweet orange, grape, and others.

Caprylic acid is a colorless oily liquid with a slightly unpleasant rancid taste. Its vapors are irritating and produce coughing when inhaled. It is very slightly soluble in water (0.068 g./100 g. at 20° C.), but it is freely soluble in ethanol, diethyl ether, chloroform, and other organic solvents.

It is commercially available as a 90% product obtained by the fractional distillation of coconut oil fatty acids. It is used as an intermediate in the manufacture of esters used in perfumery, in the manufacture of dyes, etc.

Pelargonic Acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$. Pelargonic (nonanoic) acid contains an odd number of carbon atoms and has been reported to occur free in minute quantities in human hair fat (16). If the acid is a natural product of secretion of the sebaceous glands and not an oxidation product of the C_{18} -unsaturated acids, it is the first authentic example of the occurrence of a straight-chain, odd-numbered carbon fatty acid in natural fat. It has also been reported to be present in the essential oil of *Pelargonium roseum* from which it derives its name; also in the essential oils of rue, hops, and lavender, and in Japan wax, but its presence in these products is believed to have resulted from oxidative cleavage of unsaturated acids. It has been found in a petroleum distillate, rancid (oxidized) fats, and fusel oils from beets, potatoes, and cane molasses. It is a primary

product of oxidative fission of oleic acid and other long-chain unsaturated acids with a double bond in the 9,10-position.

Pelargonic acid is an oily liquid with a rancid odor. It is almost insoluble in water (0.026 g. 100 g. at 20° C.), but is soluble in ethanol, diethyl ether, chloroform, and other organic solvents. Its melting point is 12.5° C., hence it readily crystallizes when cooled slightly. The acid is prepared by oxidizing oleic (17) and sulfated oleic acid and methyl oleate (18), and by the oxidation of undecane with nitrogen dioxide. It is claimed to be an insect repellent (19).

***n*-Capric Acid, $\text{CH}_3(\text{CH}_2)_8\text{COOH}$.** Capric (decanoic) acid occurs as a minor component in the same fats that contain caprylic acid, principally milk fats, coconut (7 to 10%) and other palm kernel oils. It is a major constituent of certain seed oils, for example, elm (50%) and California bay tree (37%). It has also been reported to be present in small quantities in the head oil of the sperm whale, in wool fat as a sterol ester (20), and free in human hair fat (16).

Capric acid is a white crystalline solid melting at 31.6° C. with an unpleasant rancid odor. It is almost insoluble in water (0.015 g./100 g. at 20° C.), but soluble in ethanol, diethyl ether, chloroform, and other organic solvents; also in dilute nitric acid (sp. gr. 1.14) from which it is precipitated unchanged by addition of water.

It is produced commercially by fractional distillation of coconut oil fatty acids and is marketed as a 90% pure product. It is used in the manufacture of esters for artificial fruit flavors and perfumes and as an intermediate for other chemical syntheses.

***n*-Hendecanoic, $\text{CH}_3(\text{CH}_2)_9\text{COOH}$.** Hendecanoic (undecylic, undecanoic) acid contains an odd number of carbon atoms. It has been reported to be present in small amounts in butter fat (21), human hair fat (16), and in the essential oil of iris, and has been found in the oxidation products of paraffin. It is a crystalline solid (m. p. 29.3° C.) with a pleasant odor unlike the lower molecular weight saturated acids.

It is produced commercially by the catalytic hydrogenation of 10-undecylenic acid, and in the laboratory from commercially available *n*-decyl alcohol. It is a powerful bactericide and undissociated molecules of the acid have a high sterilizing action against putrefying bacteria (22).

Lauric Acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$. Lauric (dodecanoic) acid is one of the three most widely distributed saturated fatty acids found in nature; the other two are palmitic and stearic. It is also the lowest saturated acid found abundantly in nature. It is found in practically all of the seed fats of the Lauraceae from which it derives its name. Some of the

seed fats of the Lauraceae contain large amounts of the acid, for example, *Litsea longifolia* in which it comprises 88% of the total fatty acids and as trilaurin, it comprises 75 to 80% of the glycerides.

Lauric acid is found in varying and often large proportions in the seed fats of the Palmae. It usually comprises 45 to 50% of the total fatty acids of coconut and the various palm kernel oils, but is seldom, if ever, present in these oils in the form of trilaurin. It occurs in cow's butter to the extent of 4 to 8%, and in the milk fats of other animals.

Lauric acid is a crystalline solid (m.p. 44.2° C.) with a faint fatty odor. It is practically insoluble in water (0.0055 g./100 g. water at 20° C.); is freely soluble in diethyl ether, but less so in ethanol (1 g./2 ml.) and propanol (1 g./2.5 ml.).

It is available commercially in the form of the mixed acids of coconut oil or as the "topped" mixture from which caproic, caprylic, and capric acids have been removed by distillation. Its principal use is as an ingredient of coconut oil base soaps, but it also finds limited use in the form of other metallic soaps (see Chapter VIII), and esters of monohydric and polyhydric alcohols. It is also used per se or in the form of its ester in the manufacture of lauroyl chloride, lauryl alcohol, lauramide, and laurionitrile. *n*-Dodecylamine, prepared by the reduction of laurionitrile, is utilized in the production of germicidal quaternary ammonium salts.

***n*-Tridecanoic Acid, $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$.** Tridecanoic acid contains an odd number of carbon atoms and its presence in natural fats has until recently been considered doubtful. It has been reported to occur in very small percentages in the oil of iris, in the free fatty acids extracted from human hair (16), and to the extent of 0.03% of the total fatty acids of butterfat (22a). It has also been found as an oxidation product of paraffin.

The synthetic acid is a crystalline solid with a rather pleasant odor. It melts at 41.5° C. and is almost completely insoluble in water (0.0033 g./100 g. water at 20° C.). There is no commercial production of the acid and it is of research interest only. It can be synthesized by several methods of which the simplest is by the hydrolysis of tridecanenitrile prepared from commercially available *n*-dodecyl bromide or chloride.

Myristic Acid, $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$. Myristic (tetradecanoic) acid is present in almost all vegetable and animal fats, usually in relatively small amounts (1 to 5%), but in a number of fats it occurs to the extent of 40 to 75% or more. It comprises 8 to 12% of the total fatty acids of milk fats and as much as 15% of the head oil of the sperm whale. In palm kernel oils it may comprise 20% of the total fatty acids. It is the pre-

dominant acid of practically all of the fats of the Myristicaceae (nutmeg family), comprising 73% of the glycerides of nutmeg (*Myristica fragans*) butter; 60 to 75% of the acids of the various *Virola* fats (ucuhuba, etc.); and 60% of the acids of *Pycanthus Kombo*. It also forms 40 to 50% of the mixed fatty acids of the various *Myrica* fats (bayberry, capeberry, candleberry, etc.).

Myristic acid is a white crystalline solid (m. p. 53.9° C.) with a slightly waxy feel. It is practically insoluble in water (0.0020 g./100 g. of water at 20° C.), sparingly soluble in cold ethanol, but soluble in methanol, diethyl ether, and other organic solvents.

It is commercially available as a fractionally distilled product of 90% purity. Its uses are similar to those of lauric acid and in addition it is used in the preparation of shaving creams, shampoos, cosmetics, and in compounding rubber, paints, and greases. It is an intermediate in the preparation of myristyl alcohol, myristoyl chloride, and related compounds.

***n*-Pentadecanoic Acid, $\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$.** Pentadecanoic acid contains an odd number of carbon atoms and like a number of other saturated acids of this type it has only recently been reported to occur in the free fatty acids extracted from human hair (16). Identification from this source was based on the melting point and neutralization equivalent of the acid regenerated from the fractionally distilled methyl esters. Subsequently it was reported to comprise 0.15% of the total fatty acids of hydrogenated mutton fat (22b), 0.82% of the total fatty acids of butterfat (22c), and 0.28% of the total fatty acids of shark (*Galeorhinus australis* Macleay) liver oil (22d). *n*-Pentadecanoic acid and an isomer of this acid have been reported to be present in menhaden oil fatty acids.

The synthetic acid is an odorless, somewhat waxy crystalline solid melting at 52.3° C. It is practically insoluble in water (0.0012 g./100 g. at 20° C.). It can be prepared from commercially available myristyl alcohol via the bromide and nitrile.

Palmitic Acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$. Palmitic (hexadecanoic) acid has been reported to be present in almost every vegetable and animal fat examined to date. On the basis of the frequency of its occurrence it may be considered as the characteristic saturated acid of natural fats. Despite its wide distribution, it is generally not present in fats in very large proportions. It is a minor component and usually forms less than 5% of the total fatty acids in the majority of fats, but in many of the common vegetable oils of commerce, such as peanut, soybean, corn, coconut and various palm kernel oils, and in many fish and other marine-animal oils.

it may comprise as much as 10% of the total fatty acids. Olive oil may contain as much as 15%, and cottonseed, avocado, and kapok oils as much as 20% or more of palmitic acid. Lard, various animal tallows, and cocoa butter contain 25 to 35%, palm oil 35 to 40%, and Chinese vegetable (stillingia) tallow 60 to 70% of this acid. It is the commonest saturated acid in the fats of aquatic animals and generally comprises about 15% of the total fatty acids from these sources.

Palmitic acid is an odorless waxy solid melting at 63.1° C. It is practically insoluble in water (0.00072 g./100 g. water at 20° C.). It is sparingly soluble in cold ethanol and petroleum naphtha, but freely soluble in hot ethanol, and in diethyl ether, propanol, and chloroform.

Palmitic acid is produced by two processes, fractional crystallization from solvents such as acetone and methanol, and fractional distillation of mixed fatty acids derived by hydrolysis of various fats. It is commercially available in the form of the distilled acid of 90% purity.

Industrially palmitic acid is used principally in the form of commercial stearic acid which is a mixture of stearic and palmitic acids containing 55% of the latter. In commercially pure form it has a variety of applications, including the preparation of esters, metallic salts, palmityl (cetyl) alcohol, amides, nitriles, amines, and quaternary ammonium salts. The acid or its derivatives find use in the manufacture of synthetic detergents, soaps, cosmetics, greases, plastics, and various types of protective and decorative coatings.

Margaric Acid, $\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$. Margaric (heptadecanoic) acid contains an odd number of carbon atoms and its occurrence as a constituent of natural fats has been a subject of much controversy. At one time its isolation was frequently reported from such sources (6), but later it was found that the acid was a mixture of palmitic and stearic acids. This misidentification arose from the fact that palmitic and stearic acids form a series of solid solutions and also a dimeric compound and a eutectic mixture at 50:50 and 70:30 mole per cent, respectively. The melting point, neutralization equivalent, and other common physical and chemical characteristics of the various solid solutions and the dimeric compound are so similar to those of margaric acid that they cannot be distinguished by these constants. They can, however be clearly differentiated by the long spacing of their x-ray diffraction patterns, a technique unknown at the time that the isolation of margaric acid was reported from natural sources.

Recently, margaric acid has been reported (16) to be a constituent of the free fatty acids extractable from human hair by diethyl ether. Iden-

tification was based on the melting point and neutralization equivalent of the acid regenerated from the fractionally distilled methyl esters. It has also been reported to be present to the extent of 1.2% in hydrogenated and unhydrogenated mutton fat (22e) and to occur along with *n*-pentadecanoic acid in shark liver oil (22d). *n*-Heptadecanoic acid and 9-heptadecenoic acid (vid.) have been isolated from the body fat of the Canadian musk ox.

Synthetic margarine acid is a waxy crystalline solid melting at 61.3° C. It is practically insoluble in water (0.00042 g./100 g. water at 20° C.), slightly soluble in ethanol, and freely soluble in diethyl ether.

The acid can be synthesized from commercially available *n*-hexadecyl (cetyl) bromide or chloride. It is principally of research interest and has been used experimentally in the form of its triglyceride in the treatment of diabetes mellitus.

Stearic Acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. Stearic (octadecanoic) acid is the highest molecular weight saturated fatty acid occurring abundantly in natural fats and oils. Although reported from fewer species of plants and animals and generally in smaller amounts than palmitic where the two acids occur together, it is nonetheless of considerable commercial importance. It occurs in small amounts in most fruit flesh and seed fats and in marine animal oils. It has also been reported (22g) to comprise somewhat more than 1% of the total acids of carnauba wax. Palm oil contains 2 to 6% of this acid; most so-called yellow oils (cottonseed, corn, soybean, peanut, sesame, sunflower, kapok) contain 2 to 8%; milk fats 5 to 15%; lard 10 to 12%; tallows 14 to 30%; cocoa and shea butters 30 to 35%. It is a principal constituent of most commercially hydrogenated fats and constitutes as much as 90% of completely hydrogenated corn and soybean oils.

Stearic acid is a waxy crystalline solid melting at 69.6° C. It is practically insoluble in water (0.00029 g./100 g. of water at 20° C.); fairly soluble in chloroform (ca. 50 g./100 ml.); and decreasingly soluble in carbon disulfide, benzene, carbon tetrachloride, ethanol, and acetone.

Stearic acid is produced commercially by several processes depending on the purity desired and the use for which it is intended. Two principal grades are the so-called "commercial or pressed" acid and distilled or solvent-crystallized acid. The first consists of a mixture of 55% palmitic acid and 45% stearic acid with varying amounts of oleic acid, and has a melting point of 55.0—55.5° C. It is produced from hydrolyzed tallow by crystallization of the mixed acids without solvent, a process known as "panning or pressing." A more homogeneous product, which con-

tains 95% or more of stearic acid, is produced by fractional distillation or crystallization from solvent of the mixed acids obtained by hydrolyzing highly hydrogenated soybean or similar oil.

The free acid finds use in the manufacture of candles, rubber articles, textiles, protective coatings, resins, pharmaceutical and toilet articles, and in metalworking. It is also used in the form of derivatives such as soaps and metallic salts, stearyl chloride or bromide, stearamide, stearonitrile, stearyl alcohol, etc.

***n*-Nonadecanoic Acid, $\text{CH}_3(\text{CH}_2)_{17}\text{COOH}$.** *n*-Nonadecanoic acid contains an odd number of carbon atoms; prior to 1955 it had not been found as a constituent of natural fats or waxes. Late in 1955, Hansen, Shorland, and Cooke (22f) reported the isolation of this acid from hydrogenated ox perinephric fat. The acid melted at 67.5–68.0° C. and gave an x-ray long spacing of 43.77 Å. The synthetic acid is a waxy crystalline solid melting at 68.6° C. It can be prepared from commercially available *n*-octyldecyl bromide or iodide by way of the nitrile. The acid has not been extensively investigated and at present is of research interest only.

Arachidic Acid, $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$. Arachidic (eicosanoic) acid is widely distributed in nature but generally it is found as a minor component in most fats. In most of the yellow oils of commerce, except peanut, it comprises 1% or less of the total fatty acids. Peanut oil contains 5 to 7% of C_{20} – C_{24} saturated fatty acids of which about one-third is arachidic. The petroleum naphtha extract of poke root is reported to contain about 6% of this acid. It is a major constituent of the seed oil or "vegetable tallow" of several members of the soapberry family (Sapindaceae). Kusum or macassar oil contains 20 to 25%, and rambutan and pulasan (*Nephelium mutabile*) tallows 20 to 35% of this acid.

Arachidic acid is also found in the depot fats of some animals and as a constituent of milk fats of various animals and in human milk fat. It has been reported to occur in the free state in the diethyl ether extract of human hair (16) and as the sterol ester in wool grease (20). It comprises 11.5% of the normal and about 4.5% of the total acids of carnauba wax (22g). It has been isolated from the fats of insects and yeasts, and from the oils of the sardine, whale, and shark's liver. It was found to comprise 1.1% of the fatty acids from an unidentified species of *Penicillium* grown on soybean lecithin (23). It has been found in appreciable amounts in hydrogenated fish oils and in a petroleum distillate.

The acid is a waxy crystalline solid melting at 75.3° C. It is practically insoluble in water, sparingly soluble in cold ethanol, but freely soluble in

hot absolute ethanol, benzene, chloroform, diethyl ether, and petroleum naphtha.

It can be prepared by hydrolysis of eicosanenitrile.

***n*-Heneicosanoic Acid, $\text{CH}_3(\text{CH}_2)_{19}\text{COOH}$.** Heneicosanoic acid contains an odd number of carbon atoms and is not known with certainty to occur in natural fats and waxes, although it has been reported as a constituent of Japan wax and peanut oil. These reports are, however, of dubious validity.

The synthetic acid is a waxy crystalline solid melting at 74.3°C . Little is known concerning the properties of this acid. It can be prepared from arachidic acid by the nitrile synthesis method or by oxidation of methyl *n*-heneicosyl ketone.

Behenic Acid, $\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$. Except for the seed oils of the Cruciferae, behenic (docosanoic) acid does not occur in the principal oils of commerce. It does occur as a minor constituent of a number of oils of the mustard family, such as ravison, 0.5%; rapeseed, 0.6 to 2.1%; mustard seed, 2.0 to 2.3%; and radish 3.4%. Sugar cane oil is reported to contain 7.6% of C_{20} – C_{24} acids, about one-third of which is believed to be behenic acid. The acid was first isolated from ben (behen) oil (*Moringa oleifera* or *M. aptera*) in which it is present to the extent of 2.7 to 6.5%. The nut oil of *Lophira alata* is reported to contain 14.2% and the seed oil of *Xylia xylocarpa* 17% of this oil.

Behenic acid has been reported to be a constituent of wool grease (20) and constitutes 9% of the normal and 3.5% of the total acids of carnauba wax (22g). It is present in montan wax and the waxes of several species of pine, also in small amounts in various milk fats, including human milk fat, and the oils of the sardine, whale, and shark liver. Large amounts of behenic acid are found in hydrogenated oil of herring, 7%; codliver, 13%; sardine, 18%; mustard seed, 46%; jamba, 50%; and rapeseed, 57%.

The acid is a waxy crystalline solid melting at 79.9°C . It is readily prepared by hydrogenation of oils containing erucic and other C_{22} -unsaturated acids.

***n*-Tricosanoic Acid, $\text{CH}_3(\text{CH}_2)_{21}\text{COOH}$.** Tricosanoic acids contains an odd number of carbon acids and is not known with certainty to occur in natural fats and waxes, although it has been reported to be present in peanut oil and in the leaf wax of the olive.

The synthetic acid is a waxy solid melting at 79.1°C . It can be prepared by the reduction of 13-ketotricosanic acid obtained by condensing the sodio derivative of ethyl 2-acetylbrassylate with stearoyl chloride.

Lignoceric Acid, $\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$. Lignoceric (tetracosanoic) acid

is widely distributed in natural fats, but usually only in very small amounts. It is the longest chain saturated fatty acid found in fats and oils and may be looked upon as the transition acid between the triglyceride fats and the monoester waxes. Lignoceric acid occurs in very small amounts in the ordinary oils of commerce: sesame, 0.4%; soybean, 0.1%; corn, 0.2% sunflower, 0.4%; rapeseed, 0.8 to 2.4%; peanut and mustard seed, ca. 1.0%; ben, 5.3%. *Cassia alata* (ringworm shrub) oil contains 15% of C_{20} – C_{24} acids most of which is believed to be arachidic. The seed fat of the condor (corail) tree (*Adenathera pavonina*) is reported to contain 25% of lignoceric acid and can be isolated in a yield of 1.5% based on the weight of the seed.

Lignoceric acid has been reported to occur as the sterol ester in wool grease (20), and in small amounts in various marine animal oils. It is the principal normal fatty acid present in carnauba wax comprising 30% of the normal and 11.5% of the total acids of carnauba wax (22g). It has been found to comprise 4% of the fatty acids of hydrogenated sardine oil and 6% of hydrogenated herring oil. It is also present in small amounts in butterfat, kidney fat, and ox spleen. It was found to constitute 3.2% of the fatty acids obtained from *Aspergillus niger* (24) and ca. 1% of the fatty acids of *Penicillium javanicum* (25). It is a constituent of certain plant waxes (carnauba), insect waxes (Chinese wax, beeswax), mineral waxes (montan), and various bacterial waxes.

Lignoceric acid is waxy crystalline solid melting at 84.2° C. It can be obtained practically in quantitative yield by the hydrolysis of tetracosanenitrile.

Pentacosanoic Acid, $CH_3(CH_2)_{23}COOH$. Pentacosanoic acid contains an odd number of carbon atoms and does not appear to be present in natural fats and waxes. The synthetic acid is a waxy crystalline solid melting at 83.5° C. Little is known concerning the properties of this acid. It can be prepared from lignoceric acid by way of pentacosanenitrile.

Cerotic Acid, $CH_3(CH_2)_{24}COOH$. Cerotic (hexacosanoic) acid has been reported to occur in practically every natural plant and insect wax examined to date. It occurs principally as the monoester of long-chain fatty alcohols. It has been reported to occur in traces in peanut, pumpkin seed, and rice oils, and in spinach fat. It is present in the form of monoesters in plant waxes (bamboo, carnauba, cotton, flax, Gedda, and certain flowers); insect waxes (Chinese wax, beeswax, stick lac); animal wax (wool grease (20)); mineral wax (montan).

Because of the difficulty of separating the higher fatty acids, quantitative determination of the percentage of the individual components in the

mixed acids derived from the hydrolysis of natural waxes has been exceedingly difficult until the development of the amplified ester distillation technique by Weitkamp (25a). When applied to the fatty acids of carnauba wax by Murray and Schoenfeld (22g) it was found that cerotic acid constituted 12% of the normal and 4.5% of the total acids.

Cerotic acid is a hard waxy solid melting at 87.7° C. A commercially pure grade acid can be prepared by fractional crystallization of the mixed acids obtained by saponification of Chinese wax, beeswax, or montan wax.

Heptacosanoic Acid, $\text{CH}_3(\text{CH}_2)_{25}\text{COOH}$. Heptacosanoic acid contains an odd number of carbon atoms and probably does not occur in natural fats and waxes. It is a crystalline solid melting at 87.6° C. It can be synthesized from 1-hexacosanol by way of the nitrile.

Montanic Acid, $\text{CH}_3(\text{CH}_2)_{26}\text{COOH}$. Montanic (octacosanoic) acid is a constituent of certain vegetable waxes (candelilla, carnauba, cotton); insect waxes (beeswax, Chinese wax); and mineral waxes (lignite, montan). Montan wax contains more than 40% of this acid and it comprises 16.5% of the normal and 6.3% of the total acids of carnauba wax (22g).

Montanic acid is a waxy crystalline solid melting at 90° C. A commercial-grade montanic acid can be prepared by fractional crystallization of the mixed acids obtained by saponification of montan wax.

Nonacosanoic Acid, $\text{CH}_3(\text{CH}_2)_{27}\text{COOH}$. Nonacosanoic acid contains an odd number of carbon atoms and probably does not occur in natural plant and insect waxes. It has been reported to occur in montan wax and in a bitumen wax derived from peat.

Nonacosanoic acid is a hard crystalline solid melting at 90.3° C. It can be prepared from montanic acid by the nitrile method of synthesis.

Melissic Acid, $\text{CH}_3(\text{CH}_2)_{28}\text{COOH}$. Melissic (triacontanoic) acid is found almost exclusively in plant (bayberry, carnauba, clematis, slash-pine, sugar cane) and insect (bee, Chinese insect, coccid, cocoon fiber, *Ceroplastes rubens*) waxes. It has also been found in montan wax and traces have been reported to occur in palm oil. It comprises 7% of the normal and 3% of the total fatty acids of carnauba wax (22g).

The acid is a hard crystalline solid melting at 93.6° C. It can be prepared by the oxidation of myricyl (melissyl) alcohol.

Hentriacontanoic Acid, $\text{CH}_3(\text{CH}_2)_{29}\text{COOH}$. Hentriacontanoic acid and the corresponding hydrocarbon, hentriacontane, contain an odd number of carbon atoms and probably do not occur in plant and insect waxes, although both substances have been reported from such sources. Reinvestigation of these waxes usually reveals that they are difficultly separable mixtures of even-numbered carbon compounds.

The synthetic acid is a hard, crystalline, waxlike solid melting at 93.1° C. It has been synthesized by oxidation of 1-triacontanol via the nitrile.

Dotriacontanoic Acid, $\text{CH}_3(\text{CH}_2)_{30}\text{COOH}$. Dotriacontanoic acid has been isolated from stick lac wax and hence is often referred to as lacceroic acid.

It is a hard waxlike solid melting at 96.2° C. The acid has been prepared by several methods including oxidation of 1-dotriacontanol; malonic ester synthesis from 1-iodotriacontane; and the reaction of *n*-docosylzinc iodide with the half ester-acid chloride of sebacic acid, reduction of the keto acid to the hydroxy acid, treatment with iodine, and removal of the latter with zinc and glacial acid.

Tritriacontanoic Acid, $\text{CH}_3(\text{CH}_2)_{31}\text{COOH}$. Tritriacontanoic acid contains an odd number of carbon atoms and probably does not occur in plant and insect waxes, although its isolation has been reported under the names psylic and ceromelissic acid from the waxes of *Ceroplastes ceriferus* and *C. rubens*.

Tetratriacontanoic Acid, $\text{CH}_3(\text{CH}_2)_{32}\text{COOH}$. Triacontanoic or geddic acid has been reported to occur in Gedda wax. It is a hard crystalline solid melting at 98.4° C. It can be prepared by the oxidation of 1-tetratriacontanol, by the Clemmensen reduction of 13-ketotetratriacontanoic acid, and from dotriacontanoic acid by the malonic ester synthesis.

Tritriacontanoic Acid, $\text{CH}_3(\text{CH}_2)_{31}\text{COOH}$. Tritriacontanoic acid contains an odd number of carbon atoms and probably does not occur in natural waxes, although it has been reported under the name ceroplastic acid to occur in olive wax and the wax from *Ceroplastes rubens*.

The synthetic wax melts at about 98.4° C. It can be synthesized from 1-tetratriacontanol by the nitrile method.

Hexatriacontanoic, $\text{CH}_3(\text{CH}_2)_{34}\text{COOH}$, and Other Higher Acids. Hexa- and octatriacontanoic, $\text{CH}_3(\text{CH}_2)_{36}\text{COOH}$, and hexatetracontanoic, $\text{CH}_3(\text{CH}_2)_{44}\text{COOH}$, acids have been prepared synthetically. Like the other long carbon-chain acids they are hard wax-like solids melting at 99.9°, 101.6°, and 106.8° C., respectively.

(b) Alkylalkanoic Acids

Prior to 1929 when Anderson (26) isolated various alkyl-branched alkanolic acids from the lipids of acid-fast bacteria only one such acid, namely, isovaleric, was known to be a constituent of natural fats. In recent years increasing numbers of branched-chain acids have been iden-

tified from natural sources, including wool fat (20), butter fat (27), mutton fat (28), and ox perinephric fat (29). A large number of such acids has also been prepared synthetically. Low molecular weight branched-chain acids (less than 7 carbon atoms) have been isolated from petroleum (30) and higher ones are believed to exist.

Most of the naturally occurring branched-chain acids have only a single branching alkyl group, generally methyl, but several polyalkyl-branched acids have been isolated and others have been prepared synthetically.

With a few exceptions which will be remarked on later, the naturally occurring monoalkyl-branched acids form two series, one of which has a methyl group attached at the penultimate position (iso acids), and the other has a methyl group attached at the antepenultimate position (anteiso acids). In the first or iso acid group the straight-chain carbon skeleton contains an odd number, and the whole molecule an even number of carbon atoms. These acids are optically inactive. In the second group the straight-chain carbon skeleton contains an even number, and the whole molecule an odd number of carbon atoms. The acids of this group are dextrorotatory. The two groups may be contrasted by their terminal groups which in the case of the iso series is isopropyl and in the anteiso series is *sym*-butyl. Klyme (30a) concluded from a consideration of the anteiso acids that the (+) anteiso-alkanoic acids are represented by a Fischer projection formula and may be termed L-methyl-substituted acids.

Wherever branched-chain acids have been found to occur in natural fats, it is in very small amounts, except in the case of isovaleric acid. The origin and natural function of these acids is obscure.

Nearly all of the branched-chain acids isolated up to the present have been from pathogenic bacteria or from animal sources, including wool grease, milk fat, ox and mutton fat, duck and goose wax, and shark liver oil. The multiplying reports of the isolation of branched-chain acids have resulted from the application of relatively new techniques such as amplified distillation with hydrocarbon diluents, chromatography, low temperature crystallization, etc.

Data for a considerable number of monoalkylalkanoic acids have been assembled in Tables 5 and 6. The more important and better known of these acids are discussed in this section.

Isobutyric Acid, $C_4H_8O_2$. Isobutyric acid, also called 2-methylpropanoic and dimethylacetic acid, $(CH_3)_2CHCOOH$, is the lowest molecular weight fatty acid that possesses a branched-chain structure. It has been

TABLE 5
Monoalkylalkanoic Acids²

Systematic name	Common or other name	Molecular formula	Structural formula, R—COOH	For- mula weight	M.p., ° C.	B.p., ^b ° C./mm.	Neu- trali- zation value	Derivative, ^c m.p. (° C.), b.p. (° C./mm.)
2-Methylpropanoic	Isobutyric	C ₄ H ₈ O ₂	(CH ₃) ₂ CH—	88.10	f.p. —47	154.4	636.79	Amide, 129; methyl ester, —84.7
2-Methylbutanoic	Active valeric	C ₅ H ₁₀ O ₂	CH ₃ CH ₂ CHCH ₃ —	102.13	<—80	174	549.34	
3-Methylbutanoic	Isovaleric	C ₅ H ₁₀ O ₂	CH ₃ CH(CH ₃)CH ₂ —	102.13	—37.6	176	549.34	Methyl ester, 116.7
Trimethylacetic	Pivalic	C ₅ H ₁₀ O ₂	(CH ₃) ₃ C—	102.13	35.5	163	549.34	Methyl ester, 102
2-Methylpentanoic	2-Methylpentylic	C ₆ H ₁₂ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)—	116.15			483.00	
3-Methylpentanoic	3-Methylpentylic	C ₆ H ₁₂ O ₂	CH ₃ CH ₂ CH(CH ₃)CH ₂ —	116.15			483.00	
4-Methylpentanoic	Isocaproic	C ₆ H ₁₂ O ₂	(CH ₃) ₃ CHCH ₂ CH ₂ —	116.15	—35	207.7	389.05	
2-Ethylhexanoic	2-Ethylcaproic	C ₈ H ₁₆ O ₂	CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)—	144.21			325.69	
4-Propylheptanoic	Propylheptylic	C ₁₀ H ₂₀ O ₂	CH ₃ (CH ₂) ₃ CH(C ₃ H ₇)(CH ₂) ₂ —	172.26		152/14	325.69	
4-Ethyloctanoic	Ethylcaprylic	C ₁₀ H ₂₀ O ₂	CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)(CH ₂) ₂ —	172.26		143/10	325.69	
2-Methyldecanoic	2-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)—	186.29		109/9	301.17	p-Bromphen- acyl ester, 67
3-Methyldecanoic	3-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₆ CH(CH ₃)CH ₂ —	186.29		154/14	301.17	p-Bromphenyl- acyl ester, 39
4-Methyldecanoic	4-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₅ CH(CH ₃)(CH ₂) ₂ —	186.29		150/10	301.17	p-Bromphenyl- acyl ester, 42
5-Methyldecanoic	5-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₄ CH(CH ₃)(CH ₂) ₃ —	186.29		168/20	301.17	p-Bromphenyl- acyl ester, 50
6-Methyldecanoic	6-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)(CH ₂) ₄ —	186.29		165/18	301.17	p-Bromphenyl- acyl ester, 51
7-Methyldecanoic	7-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)(CH ₂) ₅ —	186.29		162/15	301.17	p-Bromphenyl- acyl ester, 56
9-Methyldecanoic	9-Methylcapric	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂)CH(CH ₃)(CH ₂) ₆ —	186.29		124/2	301.17	p-Bromphenyl- acyl ester, 65.5
6-Ethylundecanoic	6-Ethylundecylic	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₂ CH(C ₂ H ₅)(CH ₂) ₄ —	186.29		166/17	301.17	
5-Propylundecanoic	5-Propylundecylic	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₃ CH(C ₃ H ₇)(CH ₂) ₃ —	186.29		167/22	301.17	
3-Methylundecanoic	3-Methylundecylic	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)(CH ₂) ₂ —	200.31		148/2	280.08	Amide, 77
6-Propylundecanoic	6-Propylundecylic	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₂ CH(C ₃ H ₇)(CH ₂) ₄ —	200.31		177/18	280.08	

2-Methylidodecanoic	$C_{13}H_{26}O_2$	$CH_3(CH_2)_9CH(CH_3)(CH_2)-$	214.34	24.1	261.75	Amide, 93
3-Methylidodecanoic	$C_{13}H_{26}O_2$	$CH_3(CH_2)_8CH(CH_3)CH_2-$	214.34		261.75	Methyl ester (130/6)
4-Methylidodecanoic	$C_{13}H_{26}O_2$	$CH_3(CH_2)_7CH(CH_3)(CH_2)_2-$	214.34	142/15	261.75	
5-Methylidodecanoic	$C_{13}H_{26}O_2$	$CH_3(CH_2)_6CH(CH_3)(CH_2)_3-$	214.34	132/10	261.75	
11-Methylidodecanoic	$C_{13}H_{26}O_2$	$CH_3CH(CH_3)(CH_2)_9-$	214.34	41.3	261.75	Amide, 97.8
7-Propyldecanoic	$C_{13}H_{26}O_2$	$CH_3(CH_2)_9CH(CH_3)(CH_2)_3-$	214.34	196/25	261.75	
2-Methyltridecanoic	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{10}CH(CH_3)-$	228.36	30	245.68	Amide, 94.5
12-Methyltridecanoic	$C_{14}H_{28}O_2$	$CH_3CH(CH_3)(CH_2)_{10}-$	228.36	53.6	245.68	Amide, 107.4
2-Methyltetradecanoic	$C_{15}H_{30}O_2$	$CH_3(CH_2)_{11}CH(CH_3)-$	242.39	40	231.46	Amide, 100
4-Methyltetradecanoic	$C_{15}H_{30}O_2$	$CH_3(CH_2)_9CH(CH_3)(CH_2)_2-$	242.39	32	231.46	
13-Methyltetradecanoic	$C_{15}H_{30}O_2$	$CH_3CH(CH_3)(CH_2)_{11}-$	242.39	51.8	231.46	Amide, 97.5
14-Methylpentadecanoic	$C_{16}H_{32}O_2$	$CH_3CH(CH_3)(CH_2)_{12}-$	256.42	62.4	218.80	Amide, 101.7
2-Ethylhexadecanoic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{11}CH(C_2H_5)-$	256.42	30	218.80	Amide, 107
2-Propyltetradecanoic	$C_{17}H_{34}O_2$	$CH_3CH(CH_3)(CH_2)_{13}-$	270.44	59.8	207.45	Amide, 98.7
2-Ethylhexadecanoic	$C_{17}H_{34}O_2$	$CH_3(CH_2)_{11}CH(C_2H_5)-$	270.44	27.5	207.45	Amide, 108
14-Ethylhexadecanoic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{10}CH(C_2H_5)-$	284.47	38	197.23	Amide, 79.9
14-Methylheptadecanoic	$C_{18}H_{36}O_2$	$CH_3CH_2CH(CH_3)(CH_2)_{12}-$	284.47	43	197.23	
15-Methylheptadecanoic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_2CH(CH_3)(CH_2)_{11}-$	284.47	43.7	197.23	Amide, 84.8
16-Methylheptadecanoic	$C_{18}H_{36}O_2$	$CH_3CH_2CH(CH_3)(CH_2)_{10}-$	284.47	68.5	197.23	Amide, 106.8
2-Butyltetradecanoic	$C_{19}H_{38}O_2$	$CH_3CH(CH_3)(CH_2)_{14}-$	284.47	30.5	197.23	Amide, 109.5
2-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{15}CH(CH_3)-$	298.49	54.7	187.96	Amide, 105.7
3-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{14}CH(CH_3)CH_2-$	298.49	52	187.96	Amide, 94
4-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{13}CH(CH_3)(CH_2)_2-$	298.49	52.5	187.96	Amide, 80.2
5-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{12}CH(CH_3)(CH_2)_3-$	298.49	48	187.96	Amide, 79.5
6-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{11}CH(CH_3)(CH_2)_4-$	298.49	45	187.96	Amide, 80
7-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{10}CH(CH_3)(CH_2)_5-$	298.49	41	187.96	Amide, 73
8-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_9CH(CH_3)(CH_2)_6-$	298.49	39	187.96	Amide, 72
9-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_8CH(CH_3)(CH_2)_7-$	298.49	36	187.96	Amide, 70
10-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_7CH(CH_3)(CH_2)_8-$	298.49	26	187.96	Amide, 79.2
11-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_6CH(CH_3)(CH_2)_9-$	298.49	8	187.96	
14-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_3CH(CH_3)(CH_2)_{12}-$	298.49	35.3	187.96	Amide, 79.3
15-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3(CH_2)_2CH(CH_3)(CH_2)_{13}-$	298.49	43.5	187.96	Amide, 79.5
16-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3CH_2CH(CH_3)(CH_2)_{14}-$	298.49	50.6	187.96	Amide, 93
17-Methylloctadecanoic	$C_{19}H_{38}O_2$	$CH_3CH(CH_3)(CH_2)_{15}-$	298.49	67.8	187.96	Amide, 102.3
15-Ethylheptadecanoic	$C_{19}H_{38}O_2$	$CH_3CH_2CH(CH_3)(CH_2)_{12}-$	298.49	37.6	187.96	
3-Methylnonadecanoic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{16}CH(CH_3)CH_2-$	312.52	48	179.52	Amide, 115
2-Ethylloctadecanoic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{15}CH(C_2H_5)-$	312.52	49.5	179.52	Ethyl ester, 22.4,
2-Methylarachidic	$C_{21}H_{42}O_2$	$CH_3(CH_2)_{17}CH(CH_3)-$	326.55	62	171.81	amide, 108

TABLE 5 (continued)

Systematic name	Common or other name	Molecular formula	Structural formula, R—COOH	Formula weight	M.p., ° C.	B.p., ° C./mm.	Neutrality value	Derivative, m.p. (° C.), b.p. (° C./mm.)
2-Propyloctadecanoic	2-Propylstearic	C ₂₁ H ₄₂ O ₂	CH ₃ (CH ₂) ₁₅ CH(C ₃ H ₇)—	326.55	46		171.81	Amide, 114.5
2-Butyloctadecanoic	2-Butylstearic	C ₂₃ H ₄₄ O ₂	CH ₃ (CH ₂) ₁₅ CH(C ₄ H ₉)—	340.57	50		164.73	Amide, 114
2-Methyldocosanoic	2-Methylbehenic	C ₂₃ H ₄₆ O ₂	CH ₃ (CH ₂) ₁₉ CH(CH ₃)—	354.60	66.9		158.22	Amide, 109.8
10-Methyltricosanoic	10-Methylbehenic	C ₂₃ H ₄₆ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)(CH ₂) ₈ —	354.60	46		158.22	Amide, 78.5
2-Pentyloctadecanoic	2-Amylsteearic	C ₂₃ H ₄₆ O ₂	CH ₃ (CH ₂) ₁₅ CH(C ₅ H ₁₁)—	354.60	49		158.22	
2-Methyltricosanoic		C ₂₃ H ₄₆ O ₂	CH ₃ (CH ₂) ₂₀ CH(CH ₃)—	368.62	68.4		152.20	
3-Methyltricosanoic		C ₂₃ H ₄₆ O ₂	CH ₃ (CH ₂) ₁₉ CH(CH ₃)(CH ₂)—	368.62	63.5		152.20	
22-Methyltricosanoic		C ₂₃ H ₄₆ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₂₀ —	368.62	83.5		152.20	Amide, 110.7
20-Ethylbehenic		C ₂₃ H ₄₆ O ₂	CH ₃ CH ₂ CH(C ₂ H ₅)(CH ₂) ₁₈ —	368.62	65.5		152.20	Amide, 90.6
18-Propylheicosanoic		C ₂₄ H ₄₈ O ₂	CH ₃ (CH ₂) ₂ CH(C ₃ H ₇)(CH ₂) ₁₈ —	368.62	52.2		152.20	Amide, 82.4
2-Hexyloctadecanoic	2-Hexylstearic	C ₂₄ H ₄₈ O ₂	CH ₃ (CH ₂) ₁₈ CH(C ₆ H ₁₃)—	368.62	53.5		152.20	
12-Hexyloctadecanoic		C ₂₄ H ₄₈ O ₂	CH ₃ (CH ₂) ₆ CH(C ₆ H ₁₃)(CH ₂) ₁₀ —	368.62	28.7		152.20	p-Bromanamide, 67.8
2-Methyltetracosanoic	2-Methylignoceric	C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₂₁ CH(CH ₃)—	382.65	72		146.62	Ethyl ester, 41
3-Methyltetracosanoic		C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₂₀ CH(CH ₃)CH ₂ —	382.65	69.1		146.62	Amide, 101
6-Methyltetracosanoic	6-Methylignoceric	C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₁₇ CH(CH ₃)(CH ₂) ₄ —	382.65	56.6		146.62	Amide, 85.3
10-Methyltetracosanoic	10-Methylignoceric	C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₁₃ CH(CH ₃)(CH ₂) ₈ —	382.65	51.5		146.62	Amide, 78.5
12-Methyltetracosanoic		C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)(CH ₂) ₁₀ —	382.65	52.2		146.62	Amide, 86.9
14-Methyltetracosanoic		C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₉ CH(CH ₃)(CH ₂) ₁₂ —	382.65	58.5		146.62	Amide, 81
18-Methyltetracosanoic		C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₆ CH(CH ₃)(CH ₂) ₁₆ —	382.65	55.8		146.62	
23-Methyltetracosanoic		C ₂₆ H ₅₀ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₂₁ —	382.65	82.6		146.62	Amide, 109
2-Heptyloctadecanoic	2-Heptylsteearic	C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₁₈ CH(C ₇ H ₁₅)—	382.65	51.5		146.62	Amide, 112
9-Octylheptadecanoic	9-Octylmargaric	C ₂₆ H ₅₀ O ₂	CH ₃ (CH ₂) ₇ CH(C ₈ H ₁₇)(CH ₂) ₇ —	382.65	14		146.62	p-Bromanamide, 80.1
24-Methylpentacosanoic		C ₂₈ H ₅₄ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₂₂ —	396.68	86.7		141.44	Amide, 112.6
2-Ethyltetracosanoic	2-Ethylignoceric	C ₂₆ H ₅₂ O ₂	CH ₃ (CH ₂) ₂₁ CH(C ₂ H ₅)—	396.68	65.5		141.44	
2-Butyldocosanoic	2-Butylbehenic	C ₂₆ H ₅₂ O ₂	CH ₃ (CH ₂) ₁₉ CH(C ₄ H ₉)—	396.68	61		141.44	
2-Hexyleicosanoic	2-Hexylarachidic	C ₂₆ H ₅₂ O ₂	CH ₃ (CH ₂) ₁₇ CH(C ₆ H ₁₃)—	396.68	65		141.44	
2-Octyloctadecanoic	2-Octylsteearic	C ₂₆ H ₅₂ O ₂	CH ₃ (CH ₂) ₁₈ CH(C ₈ H ₁₇)—	396.68	56		141.44	Amide, 113
2-Decylhexadecanoic	2-Decylpalmitic	C ₂₆ H ₅₂ O ₂	CH ₃ (CH ₂) ₁₃ CH(C ₁₀ H ₂₁)—	396.68	54		141.44	
2-Methylhexacosanoic	2-Methylcerotic	C ₂₇ H ₅₄ O ₂	CH ₃ (CH ₂) ₂₃ CH(CH ₃)—	410.70	76		136.60	Amide, 113
10-Methylhexacosanoic	10-Methylcerotic	C ₂₇ H ₅₄ O ₂	CH ₃ (CH ₂) ₁₅ CH(CH ₃)(CH ₂) ₈ —	410.70	55		136.60	Amide, 81.5
2-Nonylsteearic		C ₂₇ H ₅₄ O ₂	CH ₃ (CH ₂) ₁₈ CH(C ₉ H ₁₉)—	410.70	47		136.60	Amide, 112
2-Decylsteearic		C ₂₈ H ₅₆ O ₂	CH ₃ (CH ₂) ₁₅ CH(C ₁₀ H ₂₁)—	424.73	59		132.09	Amide, 112
2-Hendecylsteearic		C ₂₈ H ₅₆ O ₂	CH ₃ (CH ₂) ₁₅ CH(C ₁₁ H ₂₃)—	438.75	56.5		127.87	Amide, 112
2-Dodecylsteearic		C ₃₀ H ₆₀ O ₂	CH ₃ (CH ₂) ₁₈ CH(C ₁₂ H ₂₅)—	452.78	61		123.91	Amide, 112
33-Methyltetracosanoic		C ₃₃ H ₇₀ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₃₁ —	522.91	95.8		107.29	Amide, 116.7

a Source: References 78, 81, 82, and F. L. Breusch, *Fortschr. chem. Forsch.*, **1**, 567-612 (1950).

b M.L. has no measure is indicated it is atmospheric.

TABLE 6
Optically Active Monokylalkanoic Acids^a

Systematic name	Common name	Molecular formula	Structural formula, R—COOH	Formula weight	Molecular rotation, [M] _D , degree	M.p., ° C.	
						Acid	Amide
2-)-)-3-Methylpentanoic	3-Methylpentylic	C ₆ H ₁₂ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)CH ₂ —	116.15	-10.03		125.7
2-)-)-3-Methylhexanoic	3-Methylcaproic	C ₇ H ₁₄ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)CH ₂ —	130.18	+3.16	b.p. 96/4	90.5
1,4-)-)-3-Methylhexanoic	3-Methylcaproic	C ₇ H ₁₄ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)CH ₂ —	130.18	-3.18	b.p. 93/5	90.9
1,4-)-)-3-Methylheptanoic	3-Methylheptylic	C ₈ H ₁₆ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)CH ₂ —	144.21	-5.77	b.p. 80/1	81.0
1,4-)-)-3-Methylheptanoic	3-Methylheptylic	C ₈ H ₁₆ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)CH ₂ —	200.31	+10.15	b.p. 138/3	87.6
1,4-)-)-3-Methylundecanoic	3-Methylundecanoic	C ₁₂ H ₂₄ O ₂	CH ₃ (CH ₂) ₉ CH(CH ₃)CH ₂ —	214.34	+28.3	22.0	93.8
1,4-)-)-3-Methylundecanoic	3-Methylundecanoic	C ₁₂ H ₂₄ O ₂	CH ₃ (CH ₂) ₈ CH(CH ₃)CH ₂ —	242.39	+11.4	23.0	86.4
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)CH ₂ —	270.44		36.8	
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₀ CH(CH ₃)CH ₂ —	298.49	+14.5	44.1	97.7
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₉ CH(CH ₃)CH ₂ —	298.49	+0.2	13.5	76.4
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₈ CH(CH ₃)CH ₂ —	298.49	-0.15	13.4	76.3
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)CH ₂ —	298.49		35.2	101.4
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₆ CH(CH ₃)CH ₂ —	298.49	-3.01	35.2	104.4
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₅ CH(CH ₃)CH ₂ —	312.52	+13.1	47.8	
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₄ CH(CH ₃)CH ₂ —	326.55	+13.1	52.2	
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)CH ₂ —	354.60	-13.4	58.1	99.2
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)CH ₂ —	368.62		68.1	
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₉ CH(CH ₃)CH ₂ —	368.62	+15.5	62.1	101.6
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₈ CH(CH ₃)CH ₂ —	368.62	-13.0	67.8	97.6
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₇ CH(CH ₃)CH ₂ —	382.65	+13.2	65.6	102.3
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₆ CH(CH ₃)CH ₂ —	382.65	+1.1	63.7	95.6
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₅ CH(CH ₃)CH ₂ —	382.65	-3.3	60.6	92.8
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₄ CH(CH ₃)CH ₂ —	396.68	+0.4	52.8	93.3
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₃ CH(CH ₃)CH ₂ —	396.68	+1	55.6	90.0
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₂ CH(CH ₃)CH ₂ —	396.68	+2.6	56.7	93.9
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)CH ₂ —	410.70	+28.0	69.9 (74)	115.6
1,4-)-)-3-Methyltridecanoic	3-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₁₀ CH(CH ₃)CH ₂ —	424.73	+13.5	73.1	105.4

^a References 78, 81, 82, and F. L. Breusch, *Fortschr. chem. Forsch.*, **1**, 567-612 (1950).

reported to occur in carob beans (St. John's Bread), arnica root, and silique doce. It has also been reported to occur among the volatile acids of mutton fat (28a), in the rumen of the sheep (30b), and in porpoise body oil (30c). When pine oleoresin is distilled isobutyric acid, together with *n*-butyric, valeric, and caproic acids, is removed in the turpentine fraction.

Isobutyric acid is a colorless pungent liquid with an odor like butyric acid, f.p. -47.0° C., b.p. 154.4° C., sp. gr. 0.949_4^{20} , refractive index (n_D^{20}) 1.3930 . It is slightly soluble in water and completely miscible with ethanol, chloroform, and diethyl ether.

Isobutyric acid is prepared by oxidation of isobutanol or from isopropanol via chloride and nitrile. Various esters (ethyl, benzyl, and β -phenylethyl) of isobutyric acid are used as flavoring materials.

Isovaleric Acid, $C_5H_{10}O_2$. All four of the isomeric acids corresponding to $C_5H_{10}O_2$ are well known. The normal acid has already been discussed. The other three acids are isovaleric or 3-methylbutanoic (β -methylbutyric), $CH_3CH(CH_3)CH_2COOH$; α -methylbutyric (2-methylbutanoic) or methylethylacetic, $CH_3CH_2CH(CH_3)COOH$; and pivalic or trimethylacetic, $(CH_3)_3C.COOH$. Of these only isovaleric and α -methylbutyric are known to occur in nature.

Chevreul (31) first reported the isolation of isovaleric acid from the head oil of the dolphin and from porpoise oil and named it *acide phocéénique*. The most thorough examination of the natural acid was reported by André (32) who compared the products from dolphin and porpoise oils with a specimen of isovaleric acid obtained from valerian root and one prepared synthetically from isobutylmagnesium bromide and carbon dioxide. The boiling points and refractive indices of the four liquids and melting and mixed melting points of the four amides were compared. They were also compared with 50:50 mixtures of *n*-butyric and *n*-caproic acids. Although the agreement was not ideal it is evident that the acids isolated from the head oil of the dolphin and from porpoise oil by Chevreul, André, and others were indeed isovaleric acid.

Gill and Tucker (33) examined a sample of porpoise jaw oil which they claimed contained 26.7% isovaleric acid. The evidence for the presence of this acid was based on the observation that 89.6% of the mixed fatty acids, distilled at $170-171^{\circ}$ C., and the distillate fraction had zero iodine value and a neutralization equivalent of 104 (theory 102). The ethyl esters of this fraction distilled over a range of $133-145^{\circ}$ C. Since the ethyl esters of the four isomeric valeric acids distill between 133.5° and 144.6° C., the authors concluded that they had isolated an isovaleric acid

but the amount of material available did not permit them to determine unequivocally which isomer had been isolated.

Klein and Stigol (34) also reported the presence of isovaleric acid from the oil of the Black Sea dolphin. On distillation of the mixed esters a fraction boiling between 133° and 135° C. was obtained which had a characteristic fruity odor. The authors concluded that since the ethyl ester of isovaleric acid boiled at 134.3° C. and that of valeric acid at 145° C., the acid they had isolated was isovaleric. Confirmation consisted in the detection of a valerian odor of a specimen of the regenerated acid after treatment with sulfuric acid, and a ferric chloride-copper acetate test for isovaleric acid.

Isovaleric acid has been reported to occur in the free state in large amounts in valerian root; in lesser amounts in the oils of pineapple and lavender, and among the volatile acids of mutton tallow (28a), and in the rumen of the sheep (30a). It has also been isolated from porpoise body oil (30b), the hair grease of the dog (34a), the distillation products of pilot whale head oil, raw cracked gasoline, and the decomposition products of the acids extracted from gum gamboge resin (35).

The acid is formed during the high pressure synthesis of alcohols from carbon monoxide and hydrogen (36). It is prepared by the electrolytic oxidation of isoamyl alcohol (37) and the catalytic oxidation of this alcohol by carbon dioxide (38). It is also obtainable in reasonable amounts from pyroligneous acid.

Isovaleric acid is a colorless liquid with an acid taste and a disagreeable, rancid-cheese odor. Its specific gravity is 0.9314^{20} , b.p. 176° C., m.p. -37.6° C., refractive index (n_D^{40}) 1.4043 . It is slightly soluble in water (1 part in 24) and freely soluble in ethanol, chloroform, and diethyl ether.

α -Methylbutyric Acid. Active valeric or α -methylbutyric acid is the only isomer of *n*-valeric acid that is optically active and it is known in all three forms (*dextro*-, *levo*-, and racemic mixture).

The acid has been isolated from the root oil of *Angelica archangelica* (39). The dextrorotatory form, $[\alpha]_D^{21} + 17.6^{\circ}$, has been isolated from lavender oil (40), clinical penicillin (41), the volatile acids of the rumen of the sheep (30a), and the hair grease of the dog (34a). The levorotatory form has been found in the oil of champaca flowers.

dextro-Valeric acid can be prepared by oxidation of *levo*-amyl alcohol ("d-amyl alcohol," *levo*-2-methyl-1-butanol) with sulfuric acid and potassium dichromate. If *sec*-butyl carbinol from the chlorination of isoprene is used, the product is a racemic mixture of the two optically active isomers. A similar inactive mixture is obtained if the acid is prepared by

either the malonic ester or acetoacetic ester synthesis. *dl*- α -Methylbutyric acid can also be obtained by treating tetrahydrofuran with carbon monoxide at 740–800 atmospheres in the presence of a nickel carbonyl catalyst (42).

The widespread occurrence in nature of isovaleic and active valeric acids has been attributed to their formation from leucine and isoleucine by enzymic action.

Pivalic Acid. Pivalic or trimethylacetic acid has not been found in natural products but it can be prepared by a variety of reactions including (a) carboxylation of isobutylene with carbon monoxide in aqueous sulfuric acid, (b) oxidation of diisobutylene in the presence of potassium hydroxide, (c) reaction of acetone with carbon monoxide and steam in the presence of potassium hydroxide, (d) oxidation of pinacolene, (e) reaction of *tert*-butylmagnesium halides with carbon dioxide.

Pivalic acid melts at 35° C. and boils at 163° C. Its use has been patented (43) as a plasticizing agent for zein compositions having applications as impregnating agents, adhesives, and in printing inks.

Isocaproic (Isohexanoic) Acids, $C_6H_{12}O_2$. With increasing chain length the number of isomeric saturated acids becomes increasingly numerous. Seven isomers of *n*-caproic acid have been prepared. Three of the isomers may be considered as methyl-substituted pentanoic acid, namely, 2-methylpentanoic, 3-methylpentanoic or *sec*-butylacetic, and 4-methylpentanoic, $(CH_3)_2CHCH_2CH_2COOH$, which last is generally referred to as isocaproic acid. The other four isomers are 2,2-dimethyl-, 2,3-dimethyl- and 3,3-dimethylbutanoic (*tert*-butylacetic), and 2-ethylbutanoic acid. Except for 2,2-dimethyl- and 3,3-dimethylbutanoic, these isomers can be prepared by the acetoacetic or the malonic ester synthesis, although the yields are in some cases very low. Except for the isomeric valeric acids no branched-chain acids below C_9 have been found as a constituent of natural fats or waxes. Various intermediate molecular weight branched-chain acids have been synthesized and several of these have attained various degrees of industrial importance. Among these are the mixed hexanoic and decanoic acids which are synthetic mixtures principally of two or more iso acids.

Isohexanoic acids, marketed as "mixed hexanoic acids," consist of a mixture of *n*-caproic, 2-methylpentanoic, and 3-methylpentanoic acids. The product is a light-colored liquid distilling between 194° and 199° C., sp. gr. 0.9230₂₀²⁰, refractive index, n_D^{20} 1.4142.

The product has been suggested for use as an intermediate in the synthesis of flavor esters and for the preparation of polyhydroxy ester plasticizers.

2-Ethylhexanoic Acid, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COOH}$. 2-Ethylhexanoic acid has attained considerable industrial importance, especially in the form of its metallic salts (see Chapter VIII).

The acid is a liquid having a mild odor and slight solubility in water (0.25 g./100 g. water at 20°C). It is made by hydrogenating 2-ethyl-hexenal (α -ethyl- β -propylacrolein), $\text{CH}_3(\text{CH}_2)_2\text{CH}:\text{C}(\text{C}_2\text{H}_5)\text{CHO}$, to 2-ethylhexanal (α -ethyl caproaldehyde) which is catalytically oxidized in the liquid phase to the acid (44).

The free acid has been used as an insect repellent (45), in the extraction of acetic acid from dilute aqueous solutions (46), and as a plasticizer for zein compositions employed as impregnating and coating products (47). Various derivatives are used as plasticizers, for example, polyethylene glycol bis(2-ethylhexanoate) for smooth vinyl films and sheeting (48); the diester amide of 2-ethylhexanoic acid and diethanolamine for vinyl resins (49), and products from 2-ethylhexanoic acid and various amino resins (50). The esters of 2-ethylhexanoic acid and polyoxyalkylenediols are used as metal lubricants (51), and the *N*-ethylhexanoyl derivative of 3-amino-1-thiacyclopentane-1,1-dioxide has been patented as an oil additive (52).

According to Gustin, Wiberly, and Bauer (52a), 3- and 4-ethylhexanoic acid, as well as 2-*N*-propyl-, 3-*N*-propyl-, and 2-isopropylhexanoic and 2-*N*-butylhexanoic and 2-*sec*-butylhexanoic acids have been prepared together with their aluminum soaps.

Isodecanoic Acids, $\text{C}_{10}\text{H}_{20}\text{O}_2$. There is commercially available a mixture of branched-chain C_{10} -acids consisting of 96% of more isodecanoic acids. The product is a liquid distilling between 100° and 120°C . at 1 mm. pressure, sp. gr. 0.9055_{20}^{20} , refractive index, n_D^{20} 1.4357. Suggested uses for the product are the preparation of paint driers (see Chapter VIII) with improved hydrocarbon solubility, as an intermediate in the manufacture of plasticizers, and in the form of the barium salt as a stabilizer for vinyl chloride resins.

Higher Branched-Chain Acids. A number of branched-chain acids with carbon skeletons from C_9 to C_{28} have been isolated from natural sources in very small amounts. These acids can best be discussed on the basis of their sources of origin which are (a) bacteria, (b) wool fat, (c) butter fat, (d) mutton fat, and (e) ox fat.

Bacillus Acids: Tuberculostearic Acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_3)(\text{CH}_2)_8\text{COOH}$. The first branched-chain acid higher than isovaleric to be isolated from a natural fat was obtained by Anderson and Chargaff (53) in 1929, 110 years after Chevreul isolated isovaleric acid from dolphin jaw

oil. They obtained the acid from human tubercle wax. Later it was reported to be present in bovine tubercle wax (54) and in leprosy bacilli (55). Spielman (56) reported the acid to have the formula $C_{19}H_{38}O_2$ and that it corresponded to 10-methylstearic acid. It melted at $10-11^\circ C.$ and appeared to be optically inactive but it was not identical with *dl*-10-methylstearic acid which melts at $20-21^\circ C.$ However, the amides (m.p. $76-77^\circ C.$) and the tribromoanilides (m.p. $93-94^\circ C.$) of the natural and the synthetic acids were identical. Velick (57) examined the natural acid and its amide by x-rays and concluded from the observed spacing values that the acid possessed a structure corresponding to *d*- or *l*-10-methylstearic acid previously assigned to it on the basis of chemical evidence.

The structure of tuberculostearic acid was conclusively shown in 1948 by Prout *et al.* (58) and by Ställberg-Stenhagen (58a), using independent methods of synthesis, to correspond to *d*(—)-10-methyloctadecanoic acid (also written (—)-*D*-10-methyloctadecanoic acid) which was confirmed in 1951 by a third synthesis by Linstead *et al.* (58b) using the method of anodic coupling (electrochemical synthesis). All three groups prepared (+)-10- and (—)-10-methyloctadecanoic acid as well as (+)-3- and (—) 3-methylhendecanoic acid which later were used as intermediates in the preparation of the methyloctadecanoic acids.

The melting points reported for the various synthetic products ranged from $8-11^\circ C.$ to $12.8-13.4^\circ C.$ which Ställberg-Stenhagen attributes to dimorphism and changes in crystal structure which occur in the vicinity of the melting point. The reported optical rotations $[\alpha]_D^{25}$, on the other hand, were in good agreement (0.08^{22} to 0.11^{26} degrees).

Phytomonic Acid, $C_{20}H_{40}O_2$. Velick and Anderson (59) isolated from the acetone-soluble fat and from the phosphatide of the crown-gall bacillus (*Phytophthora tumefaciens*) a saturated acid, liquid at ambient temperature, which they designated phytomonic acid. The acid melted at $24^\circ C.$ and corresponded to the empirical formula $C_{20}H_{40}O_2$. Velick suggested that the acid is either 10- or 11-methylnonadecanoic acid.

Phthioic Acid, $C_{26}H_{52}O_2$. Anderson and co-workers (60,61) reported the isolation from tubercle bacilli of a polybranched-chain acid which they named phthioic acid. It melted at $20-21^\circ C.$, was optically active, $[\alpha]_D = +12.56^\circ$, and corresponded to the formula $C_{26}H_{52}O_2$. On the basis of these data they assumed the product to be a polymethylated acid, but no specific evidence was obtained with respect to the number or position of the attached methyl groups. Stenhagen and Ställberg (62) suggested that the acid was ethyldecyldodecylacetic acid, but Polgar and Robinson (63) demonstrated that this was probably incorrect and postu-

lated (64) instead that it could be either 10,13,19- or 3,12,19-trimethyltricosanoic acid, most probably the latter. Cason and Prout (65) have disagreed with the postulated structure on the basis of the high specific rotation of phthioic acid.

In addition to phthioic acid, three other branched-chain acids corresponding to $C_{24}H_{48}O_2$, $C_{25}H_{50}O_2$, and $C_{27}H_{54}O_2$ were isolated from tubercle bacilli by Ginger and Anderson (66). The three acids, like phthioic, are dextrorotatory but their complete structures were not determined. Relatively homogeneous phthioic acid, as well as the mixed acids, has been shown to produce typical tubercular lesions on injection into experimental animals.

Cason and Sumrell (67), upon re-examination of a sample of crude methyl phthioate originally prepared by Anderson, found it to be a complex mixture of at least twelve components ranging in molecular weight from C_{23} to C_{31} . It was not possible to isolate pure phthioic acid from this mixture but one fraction yielded a 2-alkyl-2-alkenoic acid which was designated C_{27} -phthienoic acid (68). Subsequently, Cason and Kalm (69) assigned a *trans*-configuration to this acid, designating it *trans*- C_{27} -phthienoic acid (see polyalkylakenoic acids).

Mycoceranic (Mycocerosic) Acid, $C_{31}H_{62}O_2$. Ginger and Anderson (70) isolated from the ether-soluble lead-salt fraction of tubercle lipids a strongly levorotatory liquid acid corresponding to the formula $C_{30}H_{60}O_2$, which they named mycocerosic acid. In the solid state it is a noncrystalline waxy product melting at $27-28^\circ C$. It has a levorotation $[\alpha]_D -5^\circ$ to -6° in chloroform. The relatively low melting point indicated that it was a branched-chain acid.

Polgar (70a) carried out various degradative studies on what appeared to be the same acid isolated from a similar source and arrived at the conclusion that it corresponded to the formula $C_{31}H_{62}O_2$ and probably was 2,4,6-trimethyloctacosanoic acid, $CH_3(CH_2)_{21}CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)COOH$. The acid was designated mycoceranic.

Wool Fat Acids. Interest in the isolation of branched-chain fatty acids from natural sources received a new impetus with the work of Weitkamp (20) on the acidic constituents of degreas (wool fat or wool wax). In addition to the previously mentioned homologous series of normal acids (*n*-decanoic to *n*-hexacosanoic) and two optically active hydroxy acids, Weitkamp isolated from wool fat two homologous series of branched-chain acids.

One series consisted of acids with a straight-chain carbon skeleton containing an odd number of carbon atoms and a branching methyl group

at the penultimate (second to last) carbon. This series of iso acids included all of the even-numbered acids from isocapric (8-methylnonanoic), $C_{10}H_{20}O_2$, to isomontanic (26-methylheptacosanoic), $C_{28}H_{56}O_2$.

The other series consisted of a group of acids with a straight-chain carbon skeleton containing an even number of carbon atoms and a branching methyl group at the antepenultimate (third to last) carbon. This series of dextrorotatory anteiso acids included all of the odd-numbered acids from 6-methyloctanoic ($C_9H_{18}O_2$) to 24-methylhexacosanoic ($C_{27}H_{54}O_2$) and 28-methyltriacontanoic ($C_{31}H_{62}O_2$).

The acids were originally present in the wool grease as sterol esters and were obtained by saponification, after which they were re-esterified and fractionally distilled to yield a series of fractions differing by one CH_2 -group. The fractions corresponding to acids with an odd number of carbon atoms each yielded an anteiso acid. Fractions corresponding to acids with an even number of carbon atoms each yielded a normal and an iso acid.

Each of the fractions of the latter series was re-esterified with methanol and redistilled in the presence of a hydrocarbon diluent which made it possible to isolate both the iso and normal acids. Each acid was identified by its melting point, mixed melting point, melting point curves, melting point of its amide, and by dark field photomicrographs.

Tiedt and Truter (71) isolated from a wool grease sludge 24-methylhexacosanoic acid, $[\alpha]^{18} + 1.5$ ($CHCl_3$); 26-methyloctacosanoic acid, m.p. $76.1^\circ C$, $[\alpha]^{18} + 1.8$ ($CHCl_3$), amide m.p. $102.8^\circ C$; and 28-methyltriacontanoic acid, $[\alpha]^{18} + 3.0$ ($CHCl_3$ sol.). Horn *et al.* (72) reported the isolation of 16-methylheptadecanoic acid from the saponifiable fraction of wool wax.

Data relating to the properties of the wool wax branched-chain acids which were compiled by Truter (71a) are given in Tables 7 and 7a.

Butterfat. In 1951 Shorland and co-workers (73a) of the Department of Scientific and Industrial Research, Wellington, New Zealand, announced the isolation from hydrogenated butterfat of a branched-chain fatty acid melting at $33.5^\circ C$. and corresponding to the formula $C_{18}H_{36}O_2$. This report was followed shortly by another (73b) announcing the isolation from butterfat of two C_{17} methyl-branched acids, one of which melted at $54.4^\circ C$. and appeared to be an anteiso acid. These announcements were followed in turn by another reporting the presence of a multi-branched C_{20} -acid having three and possibly four branching methyl groups (73c). During the succeeding several years this group of workers reported the isolation from butterfat of an extensive series of iso and anteiso branched-chain acids among which were the following:

TABLE 7
Wool Wax Alkylalkanoic (Iso Series) Acids^a (M.P., °C.)

Carbon chain	Approximate % in the total acids	Wool wax acid	Synthetic acid	Wool wax amide	Synthetic amide	Synthetic ^b		
						<i>p</i> -Bromophenyl ester	Anilide	Benzimidazole
8			b.p. 129/15 mm. ^b		114.6 ^b	67.7		
10	0 1		24 0, ^c 19.0 ^b	103.1 ^d	103.8, ^c 103.0 ^b	68.0	90.3	156.3
12	0 3	41.2 ^d	41.4, ^c 41.0 ^b	108.0 ^d	108.4, ^c 105.7 ^b	70.3	64.8	
14	2 2	53.3 ^d	50.5, ^c 53.6, ^f 53.6, ^e 52.0 ^b	107.3 ^d	108.3, ^c 108.5, ^b 107.8 ^f	72.0	75.1	
16	4 5	62.4 ^d	62.4, ^e 61.6, ^f 62.0 ^b	102.1 ^d	101.7, ^f 102.8 ^b	77.0	82.2	101.5
18	3 1	69.5 ^d	68.5, ^f 68.2, ^e 69.7, ^c 68.0 ^b	107.3 ^d	107.8, ^c 106.8, ^e 106.5 ^b	80.0	87.3	98.5
20	3 9	75.3 ^d	75.6, ^c 75.1 ^b	105.1 ^d	106.1, ^c 103.0 ^b	80.9	88.6	
22	3 1	75.0 ^g						
		79.4 ^d	79.5 ^b	108.4 ^d	108.5 ^b	84.2	87.3	91.5
24	2 2	80.2 ^g						
		83.1 ^d	83.5, ^f 83.2 ^b	110.5 ^d	110.7, ^f 110.8 ^b	85.2	91.4	
26	2 8	83.4 ^g						
		86.9 ^d	86.7, ^f 87.2 ^b	112.1 ^d	112.6, ^f 112.6 ^b	81.6	89.6	
28	0 6	86.3 ^g						
		89.3 ^d	89.0 ^b			83.8		

^a Adapted from E. V. Truter, *Wool Wax Chemistry and Technology*, Cleaves-Hume, London, 1956.

^b A. H. Millburn and E. V. Truter, *J. Chem. Soc.*, 1954, 3344-3351.

^c F. W. Hogen, D. Ilse, D. A. Sutton, and J. P. de Villiers, *J. Chem. Soc.*, 1953, 98-102.

^d A. W. Weitkamp, *J. Am. Chem. Soc.*, 67, 447-454 (1945).

^e C. R. Fordyce and J. R. Johnson, *J. Am. Chem. Soc.*, 55, 3368-3372 (1933).

^f E. Stenhagen and B. Tägtström-Eketorp, *Arkiv Kemi, Min. Geol.*, 19A, No. 8, 1-10 (1945); K. E. Arosenius, G. Stållberg, E. Stenhagen, and B. Tägtström-Eketorp, *ibid.*, 26A, No. 19, 1-20 (1949).

^g K. E. Murray and R. Schoenfeld, *J. Am. Oil Chemists' Soc.*, 29, 416-420 (1952).

TABLE 7a
Wool Wax Alkylalkanoic [(+)-Anteiso Series] Acids^a (M.p., ° C.)

Car- bon chain	Approximate % in the total acids	Wool wax acid	Synthetic acid	Wool wax amide	Synthetic ^b			
					Synthetic amide	p- Bromo- phen- acyl ester	Anilide	Benzimid- azole
9	0.1	b.p. 60/2 mm. ^c	b.p. 149/21 mm., ^d b.p. 138/10 mm., ^b b.p. 156/10 mm., ^b	89.7 ^c	91.6, ^{e,f} 91.0, ^d 90.1 ^b	59.3		
11	0.5	-18.5 ^c	5.8 ^b	87.1 ^c	87.2, ^{e,g} 86.9 ^b	50.1	77.1	99.8
13	0.8	6.2 ^c	22.8 ^b	92.4 ^c	92.1, ^{e,g} 90.0 ^b	56.0		
15	3.8	23.0 ^c	40.1, ^{e,g} 36.8, ^h 36.0 ^b	86.4 ^c	85.0, ^{e,g} 86.3 ^b	59.3	58.3	120.0
17	2.8	36.8 ^c		90.9 ^c	89.5, ^h 90.6, ^{e,g} 91.1 ^b	64.2	61.6	96.4
		37.2 ⁱ						
19	3.8	46.8 ^c	50.6, ^{e,f} 48.5 ^b	93.2 ^c	93.0, ^{e,f} 93.6 ^b	71.2	68.3	
		46.3 ^b						
21	4.5	55.6 ^c	57.6, ^{e,g} 55.3 ^b	94.1 ^c	93.4, ^{e,g} 94.6 ^b	75.6	74.1	
		55.8 ⁱ						
23	2.8	62.1 ^c	61.5 ^b	99.9 ^c	99.0 ^b	80.0	79.4	
		62.1 ⁱ						
25	5.6	67.8 ^c	67.8 ^b			82.6		
		68.1 ⁱ						
27	4.2	72.9 ^c						
		73.6 ⁱ	72.1 ^b	104.5 ^c	104.9 ^b	86.7		
		72.5 ^j		101.3 ^j				
29	-1.0	76.1 ^j	76.5 ^b	102.8 ^j				
31		80.7 ^c	80.3 ^b	107.0 ^c	107.3 ^b	86.4	92.6	
		78.8 ^j		107.5 ^j				

Methyldodecanoic Acid, $C_{13}H_{26}O_2$. (+)-10-Methyldodecanoic, 11-methyldodecanoic, and *n*-tridecanoic acids were found to comprise 0.01%, 0.05%, and 0.03%, respectively, of the total fatty acids of butterfat (73d).

Methyltridecanoic Acid, $C_{14}H_{28}O_2$. 12-Methyltridecanoic acid was found to constitute about 0.05% of the total fatty acids of butterfat (73e).

Methyltetradecanoic Acid, $C_{15}H_{30}O_2$. (+)-12-Methyltetradecanoic and 13-methyltetradecanoic acids together with *n*-pentadecanoic acid were found to be present to the extent of 0.43, 0.37, and 0.82%, respectively, in the total fatty acids (73f, 73g). These acids had previously been isolated from mutton fat.

Ox Fat. The New Zealand group of workers have reported the isolation of two branched-chain fatty acids from hydrogenated ox fat. One acid corresponds to the empirical formula $C_{16}H_{32}O_2$ and the other to $C_{17}H_{34}O_2$; both are members of the iso series of branched-chain acids.

Methylpentadecanoic Acid, $C_{16}H_{32}O_2$. 14-Methylpentadecanoic (isopalmitic) acid was isolated in an amount equivalent to 0.1% of the total fatty acids of hydrogenated ox perinephric fat (74a).

Methylhexadecanoic Acids, $C_{16}H_{34}O_2$. In 1952 Hansen *et al.* (74b) reported the presence of a C_{17} -methyl-branched saturated fatty acid isomeric with *n*-heptadecanoic acid in the fat extracted from ox suet. In a subsequent publication (74c), reporting the isolation of 15-methylhexadecanoic acid from hydrogenated ox perinephric fat, it was stated that the previously isolated acid was anteiso-14-methylhexadecanoic acid. The 15-methyl-substituted acid was reported to comprise 0.06% of the total fatty acids of the ox fat.

Mutton Fat. In the course of their investigations of the occurrence of branched-chain acids in natural fats, the New Zealand research group isolated from mutton fat a C_{13} -anteiso acid, a C_{15} -iso and a C_{15} -anteiso acid, as well as a normal C_{15} -acid; a C_{17} -acid; also a C_{17} -iso acid, a C_{17} -multibranched acid, and a C_{17} -normal acid. The occurrence of the normal acids from this source was remarked on earlier in this chapter.

^a Adapted from E. V. Truter, *Wool Wax Chemistry and Technology*, Cleaver-Hume, London, 1956.

^b A. H. Millburn and E. V. Truter, *J. Chem. Soc.*, 1954, 3344-3351.

^c A. W. Weitkamp, *J. Am. Chem. Soc.*, 67, 447-454 (1945).

^d L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 2685-2689.

^e *dl*-Form.

^f J. Cason and F. S. Prout, *J. Am. Chem. Soc.*, 66, 46-50 (1944).

^g J. R. Nunn, *J. Chem. Soc.*, 1951, 1740-1744.

^h S. F. Velsck and J. English, Jr., *J. Biol. Chem.*, 160, 473-480 (1945).

ⁱ K. E. Murray and R. Schoenfeld, *J. Am. Oil Chemists' Soc.*, 29, 416-420 (1952).

^j J. Tiedt and E. V. Truter, *Chem. & Ind.*, 1952, 403.

Methyldodecanoic Acid, $C_{13}H_{26}O_2$. Hansen, Shorland, and Cooke (75a) isolated from the external carcass fat of the sheep the C_{13} -anteiso acid, namely, C_{10} -methyldodecanoic, melting at 4° C. and having a refractive index 1.4424_D^{25} .

Methyltetradecanoic Acid, $C_{15}H_{30}O_2$. (+)-12-Methyltetradecanoic and 13-methyltetradecanoic acids were isolated from the external fatty tissue of the sheep. The optically active acid which melted at 25.8° C. was estimated to be present in excess of 0.04% of the total fatty acids, and the 13-methyl-substituted acid (m.p. 50.2° C.) comprised ca. 0.02%. The latter acid is an exception to statement concerning the nature of carbon skeleton of the natural iso acids. The 13-methyltetradecanoic acid contains a straight chain with an even number of carbon atoms and the whole molecule an odd number of carbon atoms. Hansen and Shorland (73b) previously isolated from butterfat a similar anomalous iso acid.

Methylhexadecanoic Acid, $C_{17}H_{34}O_2$. Two branched-chain acids, isomeric with margaric acid, were isolated from mutton fat. One of these was (+)-14-methylhexadecanoic acid (75). The other acid, representing 0.01% of the total fatty acids, melted at -8° C., was weakly levorotatory $[\alpha]_D^{21} -0.3$ ($CHCl_3$), refractive index 1.4518_D^{20} , and had a C-methyl content equivalent to two methyl groups. The positions of the methyl groups were not established (75).

Other Sources of Branched-Chain Acids. Weitzel (76) reported the occurrence of branched-chain saturated fatty acids in the wax glands of the duck and goose. The fatty acids of the wax gland of the duck contained one-third straight-chain and two-thirds branched-chain acids; 36% of the acids were steam-volatile, optically active, branched-chain with molecular weights between C_7 and C_{10} . The nonvolatile fraction also contained optically active, branched-chain acids with molecular weights between C_{10} and C_{18} , principally methylhexanoic and methylheptanoic.

The fatty acids of the wax gland of the goose did not contain a steam-volatile fraction but yielded large amounts of branched-chain acids with molecular weights between C_{13} and C_{18} , consisting principally of methyl-dodecanoic and methyltridecanoic acids.

In 1952 Morice and Shorland (77) reported the isolation of a C_{18} -multibranched acid from shark (*Gelcorhinus australis*) liver oil, but did not determine its structure. In 1956 they reported the isolation of 13-methyltetradecanoic, (+)-12-methyltetradecanoic, 15-methylhexadecanoic, and (+)-14-methylhexadecanoic acids from the same source.

Synthetic Branched-Chain Acids. Because of the small amounts of branched-chain acids that are present in the mixed fatty acids of natural

fats and the difficulties encountered in isolating and purifying them, most of our knowledge of the properties of these acids has been derived from synthetic products. Various workers have contributed to the rapidly growing body of knowledge in this field of fatty acid chemistry. Foremost among the contributors to this field has been Prof. James Cason (78), formerly at Vanderbilt University and presently at the University of California. Cason began his researches in this field in 1941 and has contributed more than 30 publications which are to be found principally in the *Journal of Organic Chemistry*.

Gunther Weitzel in Germany has contributed largely to this field through the preparation of various methyl-substituted fatty acids including the entire series of methylpalmitic (79) and methylstearic acids (80). The Stenhagens (81) in Sweden and Milburn and Truter (81a) in England have also contributed extensively to this field. The last-mentioned workers prepared twelve members of the iso series (up to C_{25}) of methyl-branched saturated acids and thirteen members of the (+)-anteiso series (up to C_{31}) by the method of anodic coupling. They also reduced the acids to the corresponding alcohols and prepared various derivatives of both the acids and alcohols. Among others who have contributed to this field may be mentioned Chargaff (81b), who synthesized a series of 2-substituted hexacosanoic acids; Schneider and Spielman (81c), who synthesized a series of 2-methyl and 10-methyl-substituted fatty acids containing 27 carbon atoms; and Birch and Robinson (81d), who prepared a number of long-chain substituted acetic and propionic acids. Buu-Hoï and Cagniant (82) have described the preparation and properties of most of the 2,2-dimethyl-substituted saturated acids from 2,2-dimethylecaprylic to 2,2-dimethylhendecanoic. In general, the last-mentioned disubstituted acids are oily liquids distillable only under reduced pressure. Polgar and Robinson (63) synthesized a series of tri-substituted acetic and other branched-chain acids.

Data with reference to the melting points and other properties of the various synthetic branched-chain fatty acids are given in Tables 5 to 8. General methods for the synthesis of these acids are given in Chapter XVIII and a discussion of their crystal properties will be found in Chapter IV.

(c) Monohydroxyalkanoic Acids

Investigations during the past decade have indicated that hydroxy acids, both saturated and unsaturated, occur more frequently as constituents of

TABLE 8
Polyalkylalkanoic Acids^a

Systematic name	Common name	Molecular formula	Structural formula, R—COOH	For- mula or weight	M.p. or b.p., ° C. or ° C./mm.	Derivative, m.p., ° C.
2-Butyl-5-methylpentanoic	2-Butyl-5-methyl-pentyl	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₂ CH(CH ₃)—	172.26	137/10	
2-Isobutyl-5-methylpentanoic	2-Isobutyl-5-methyl-pentyl	C ₁₀ H ₂₀ O ₂	CH ₃ (CH ₂) ₂ CH[CH(CH ₃) ₂ CH ₂]—	172.26	137/10	
2,3-Dimethylnonanoic	2,3-Dimethylnonyl	C ₁₁ H ₂₂ O ₂	C(CH ₃) ₂ CH(CH ₃)CH(CH ₃)—	186.29	142/5	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 22
4,8-Dimethylnonanoic	4,8-Dimethylnonyl	C ₁₁ H ₂₂ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₃ CH(CH ₃)(CH ₂)—	186.29	157/15	<i>p</i> -Bromphenacyl ester, 36
2-Butyl-5-methylhexanoic	2-Butyl-5-methyl-caproyl	C ₁₁ H ₂₂ O ₂	CH ₃ CH(CH ₂) ₂ CH(CH ₂) ₂ CH(CH ₃)—	186.29	138, 10	
4,4-Dimethyldecanoic	4,4-Dimethylcapryl	C ₁₂ H ₂₄ O ₂	CH ₃ (CH ₂) ₃ C(CH ₃) ₂ (CH ₂) ₂ —	200.31	157, 10	5-Benzylthiuronium salt, 133
2-Ethyl-3-methylnonanoic	2-Ethyl-3-methylnonyl	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)CH(CH ₂)—	200.31	145/5	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 138
2,2-Dimethyl-4-ethyloctanoic	2,2-Dimethyl-4-ethylcapryl	C ₁₂ H ₂₄ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₂) ₂ CH ₂ C(CH ₃) ₂ —	200.31	169/20	
2-Propyl-3-methylnonanoic	2-Propyl-3-methylnonyl	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₃ CH(CH ₃)CH(CH ₂)CH ₂ —	214.34	136/1	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 131
2,2-Dimethyldodecanoic	2,2-Dimethyl-lauric	C ₁₄ H ₂₈ O ₂	CH ₃ (CH ₂) ₉ C(CH ₃) ₂ —	228.36	4	
2-Butyl-3-methylnonanoic	2-Butyl-3-methylnonyl	C ₁₁ H ₂₂ O ₂	CH ₃ (CH ₂) ₆ CH(CH ₃)CH(CH ₂)CH ₂ —	228.36	162/3	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 108
2-Butyl-2-ethylnonanoic	2-Butyl-2-ethylnonyl	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₆ C(CH ₃) ₂ C(CH ₃)—	242.39		<i>p</i> -Bromanalide, 89
3-Ethyl-3-butylnonanoic	3-Ethyl-3-butyl-nonyl	C ₁₅ H ₃₀ O ₂	CH ₃ (CH ₂) ₅ C(CH ₃) ₂ C(CH ₃)CH ₂ —	242.39	141/1	<i>p</i> -Bromanalide, 89
4-Butyl-4-ethylnonanoic	4-Butyl-4-ethylnonyl	C ₁₃ H ₂₆ O ₂	CH ₃ (CH ₂) ₄ C(CH ₃) ₂ C(CH ₃)CH ₂ —	242.39		<i>p</i> -Bromanalide, 122.2
3,7,11-Trimethyldodecanoic	3,7,11-Trimethyl-lauric	C ₁₆ H ₃₂ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₃ CH(CH ₃)(CH ₂) ₃ CH(CH ₃)CH ₂ —	242.39	liq.	

2,3-Dimethyl-2-octadecanoic	2,2-Dimethylmyristic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_4C(CH_3)_2(CH_2)_7-$	256.42	215.16	S-Benzylthio- nium salt, 134
3,3-Dimethyltetradecanoic	3,3-Dimethylmyristic	$C_{14}H_{28}O_2$	$CH_3(CH_2)_6C(CH_3)_2CH_3-$	256.42	15	
4,4-Dimethyl-4-octadecanoic	4,4-Dimethylmyristic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_9C(CH_3)_2(CH_2)_7-$	256.42	205.10	
2-Butyl-2-pentylheptanoic	2-Butyl-2-amylheptylic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_4(C_4H_9)(C_5H_{11})-$	256.42	160.2	
1,4,4-Dimethylpentadecanoic	α -Neopentylauric	$C_{17}H_{34}O_2$	$CH_3C(CH_3)_2(CH_2)_{12}-$	270.44	43.3	Amide, 104.0
3-Methyl-2-heptylnonanoic	3-Methyl-2-heptylnonylic	$C_{17}H_{34}O_2$	$CH_3(CH_2)_5CH(CH_3)C(CH_3)(CH_2)_{11}-$	270.44	60	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 102
2,2-Dipentylheptanoic	2,2-Diamylheptylic	$C_{17}H_{34}O_2$	$CH_3(CH_2)_4(C_5H_{11})_2-$	270.44	168.2	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 99
2,2-Dimethylhexadecanoic	2,2-Dimethylpalmitic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{13}C(CH_3)_2-$	284.47	42	
2-Octyl-3-methylnonanoic	2-Octyl-3-methylnonylic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_5CH(CH_3)CH(C_8H_{17})-$	284.47	64	Bis(<i>p</i> -dimethyl-aminophenyl)-ureid, 92
2,3-Dimethylheptadecanoic	2,3-Dimethylmargaric	$C_{19}H_{38}O_2$	$CH_3(CH_2)_{13}CH(CH_3)CH(CH_3)-$	298.49	43	Amide, 80; <i>p</i> -bromanilide, 85.4
2-Methyl-2-octyldodecanoic	2-Methyl-2-octylcapric	$C_{19}H_{38}O_2$	$CH_3(CH_2)_7(CH_3)C(CH_3)H_{17}-$	298.49	235.12	
2,2-Dimethyloctadecanoic	2,2-Dimethylstearic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{15}C(CH_3)_2-$	312.52	58	Amide, 58.5; <i>p</i> -bromanilide, 89.7
2,3-Dimethyloctadecanoic	2,3-Dimethylstearic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{14}CH(CH_3)CH(CH_3)-$	312.52	64	Amide, 118.2
2,4-Dimethyloctadecanoic	2,4-Dimethylstearic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{13}CH(CH_3)CH_2CH(CH_3)-$	312.52	39	
(+)-2,9-Dimethyloctadecanoic ^b	2,9-Dimethylstearic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_8CH(CH_3)(CH_2)_6CH(CH_3)-$	312.52	34	Amide, 90.8
3,3-Dimethyloctadecanoic	3,3-Dimethylstearic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_{14}C(CH_3)_2CH_2-$	312.52	44.8	Amide, 58.3 and 39
2-Butyl-2-heptylnonanoic	2-Butyl-2-heptylnonylic	$C_{20}H_{40}O_2$	$CH_3(CH_2)_6(C_4H_9)C(CH_3)(C_7H_{15})-$	312.52	179.1	
(+)-2,3-Dimethylheicosanoic ^c		$C_{22}H_{44}O_2$	$CH_3(CH_2)_{17}CH(CH_3)CH(CH_3)-$	354.60	65.8	Amide, 58.3 and 39
(-)-2-Methyl-2-ethyl-20,50-Dimethylheicosanoic ^c	2-Methyl-2-ethyl-arachidic	$C_{22}H_{44}O_2$	$CH_3(CH_2)_{17}(C_2H_5)C(CH_3)-$	354.60	54.4	
20,20-Dimethylheicosanoic ^c		$C_{22}H_{44}O_2$	$CH_3(CH_2)_{15}CH(CH_3)(CH_2)_2CH(CH_3)-$	354.60	28.5	Amide, 98.3
20,20-Dimethylheicosanoic ^c		$C_{22}H_{44}O_2$	$CH_3C(CH_3)_2(CH_2)_{18}-$	354.60	63.3	

TABLE 8 (Continued)

Systematic name	Common name	Molecular formula	Structural formula, R-COOH	For- mula weight, ° C./mm.	M.p. or b.p., ° C.	Derivative m.p., ° C.
(+)-3,4-Dimethylidococ- sanoic ^f	3,4-Dimethylbehenic	C ₃₄ H ₅₈ O ₂	CH ₃ (CH ₂) ₁₇ CH(CH ₃)CH(CH ₃)CH ₂ —	368.62	50.4, 49.6	Amide, 82.4, 95.1
13,16-Dimethyltricosanoic		C ₃₅ H ₆₀ O ₂	CH ₃ (CH ₂) ₆ CH(CH ₃)(CH ₂) ₂ CH(CH ₃)(CH ₂) ₁₁ —	382.65	15	Amide, 57
(+)-2L,9L-Dimethyltetra- cosanoic	2,9-Dimethylig- noric	C ₃₆ H ₆₂ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)(CH ₂) ₆ CH(CH ₃)—	396.68	34.8	Amide, 90.8
(+)-2L,9D-Dimethyl- tetracosanoic	2,9-Dimethylig- noric	C ₃₆ H ₆₂ O ₂	C'H ₃ (CH ₂) ₁₁ CH(CH ₃)(CH ₂) ₆ CH(CH ₃)—	396.68	20.2	Amide, 87.3
(-)-3L,6D-Dimethyltetra- cosanoic ^g	3,6-Dimethyliz- noric	C ₃₆ H ₆₂ O ₂	CH ₃ (CH ₂) ₁₇ CH(CH ₃)(CH ₂) ₂ CH(CH ₃)CH ₂ —	396.68	45, 41, 34	Amide, 83.9, 88.4
14,17-Dimethyltetra- sanoic	14,17-Dimethyliz- noric	C ₃₆ H ₆₂ O ₂	CH ₃ (CH ₂) ₆ C'H(CH ₃)(CH ₂) ₂ CH(CH ₃)(CH ₂) ₁₂ —	396.68	20	Amide, 62
3,13,19-Trimethyltrico- sanoic		C ₃₉ H ₆₆ O ₂	C'H ₃ (CH ₂) ₃ CH(CH ₃)(CH ₂) ₃ C'H(CH ₃)(CH ₂) ₉ CH(CH ₃)CH ₂ —	396.68	208.0, 1	Amide, 37
3,13-Dimethylpentaco- sanoic		C ₄₂ H ₈₀ O ₂	C'H ₃ (CH ₂) ₁₁ (C'H ₃)(CH ₂) ₉ CH(CH ₃)CH ₂ —	419.70	227.0, 1	Amide, 85

^a References 81, 82 and F. L. Breusch, *Fortschr. chem. Forsch.*, **1**, 567-612 (1950).^b [M]_D²⁵ + 30°.^c [M]_D²³ + 66°.^d [M]_D²³ - 15.2°.^e Diastereoisomeric mixture of 2p,5p, and 2L,5p.^f Two dextrorotatory diastereoisomers [M]_D²⁴ + 31.3° and [M]_D²⁵ + 19.7°, respectively.^g The acid is trimorphic and the amide dimorphic indicated by the multiple melting points.

natural lipids than was formerly thought to be the case. The lower molecular weight hydroxy acids are found in nature but not as constituents of fats and waxes. The most widely occurring of the lower acids is lactic, an acid of considerable commercial importance.

Higher molecular weight hydroxy acids have been shown to be present in various natural waxes (beeswax, caranday, candellila, carnauba, licuri or ouricury, conifer waxes, jalop, tree-bark waxes, wool wax), as constituents of brain lipids (cerebrosides), and in some seed fats. Hydroxy acids are also sometimes found in normal fats and oils, probably as a result of atmospheric oxidation. Occasionally they may form precipitates in fatty oils after long standing especially when exposed to light and elevated temperatures.

The hydroxyl group may be attached at any point of the hydrocarbon chain of a saturated fatty acid, hence the number of possible position isomers increases with the chain length; in any given acid it is one less than the number of carbon atoms in the chain. More than one hydroxyl group may be present in the substituted acid. Acids containing from one to six hydroxyl groups have been isolated from natural sources or have been prepared synthetically.

The presence of one or more hydroxyl groups markedly affects the chemical and physical properties of the substituted acid compared to the corresponding normal acid. The presence of a hydroxyl group introduces asymmetry in the molecule and therefore induces optical activity.

The monohydroxy acids are relatively stable although the 4-hydroxy and 5-hydroxy acids are stable only at low temperatures. The inner lactones formed by slight heating of the aforementioned hydroxy acids melt about 40° below the corresponding acids. Hydroxy acids may be dehydrated to form unsaturated acids and in some cases they may form etholides, that is, linear esterification products which have the properties of alcohols, esters, and acids.

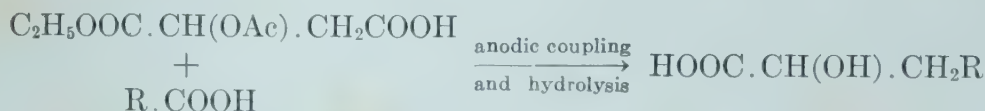
The melting points of the hydroxy acids are higher than the corresponding acids, and their solubilities in water are increased, whereas their solubilities in diethyl ether, petroleum hydrocarbons, and to some extent in ethanol are depressed. Branching in the chain of the hydroxy acid or the presence of normal acids in a solution increases the solubility of the former.

Monohydroxy acids can be prepared by (a) the action of aqueous alkali hydroxides on halogen-substituted fatty acids, although the reaction may be accompanied by dehalogenation to yield an unsaturated acid or by

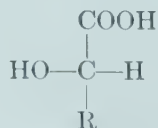
lactone formation: (b) addition of sulfuric acid to the double bonds of mono-unsaturated acids followed by hydrolysis of the sulfated acid which yields two isomers often difficult to separate; and (c) reduction of mono-keto acids.

All of the possible position isomers of the monohydroxy saturated acids from hydroxyacetic to hydroxycaproic have been synthesized although a number of them have not been well characterized. Of the higher molecular weight acids, the α - and the ω -hydroxy acids have been synthesized, but many of the intermediate substituted acids are unknown. An exception to this statement is the series of hydroxystearic acids, all of which have been synthesized and their thermal and x-ray characteristics determined.

The configurational correlation of the optically active α -hydroxy acids is unusually difficult, according to Horn and Pretorius (83), because higher homologs cannot be derived from lower ones by applying conventional methods of chain building to the carboxyl group, and partly because other chemical methods, which have been used for the correlation of the lower homologs, are laborious with higher homologs. Because of these difficulties and the interest of Horn *et al.* in the hydroxy acids of wool fat they devised a simple synthetic method of anodic coupling of an optically active form of monoethyl ester of acetylmalic acid with the appropriate normal carboxylic acid to produce 2-hydroxybutanoic, 2-hydroxyhexanoic, 2-hydroxyoctanoic, 2-hydroxydecanoic, and 2-hydroxyhexadecanoic acids in the following manner:



Horn and Pretorius measured the optical rotation of the end products, their sodium salts, and methyl esters in various solvents and reported a number of physical constants for each. All of the above-mentioned hydroxy acids which were prepared from (—)-malic acid had the configuration



and by analogy with the amino-acid convention were denoted L_s , i. e., L_s -2-hydroxybutanoic acid, L_s -2-hydroxyhexanoic acid, etc.

The melting points of the monohydroxyalkanoic acids from C_{12} to C_{34} and their methyl esters are given in Table 9.

Hydroxyacetic Acid, CH_2OHCOOH . Hydroxyacetic or glycolic acid is the lowest member of the series of hydroxyalkanoic acids. It has been found in nature in sugar beets and unripe grapes. It is a colorless, translucent, odorless solid which melts at $79\text{--}80^\circ\text{C}$. It also exists in a metastable form melting at 63°C . which forms spontaneously when the supercooled liquid is held at 30°C ., but reverts to the stable form. It is slightly volatile with steam but cannot be distilled even in a vacuum because it readily undergoes self-esterification to form polyglycolide.

Glycolic acid is produced commercially as an intermediate in the manufacture of ethylene glycol and is available in the form of a 70% aqueous solution. It is employed in the textile and tanning industries, for bright-dipping copper prior to drawing into wire, electropolishing stainless steel, and in acid-washing milk cans and dairy machinery (84).

Hydroxypropionic (Hydroxypropenoic) Acids, $\text{C}_3\text{H}_6\text{O}_3$. Both of the positional isomeric hydroxypropionic acids are known, namely, 2-hydroxypropionic or lactic acid, $\text{CH}_3\text{CHOHCOOH}$, and 3-hydroxypropionic acid or hydraacrylic (ethylene lactic) acid, $\text{CH}_2\text{OHCH}_2\text{COOH}$. The latter is of limited occurrence in nature and of little industrial importance.

Lactic acid, the alpha isomer, is the simplest hydroxy acid containing an asymmetric carbon atom and it exists in two optically active forms and a racemic modification. All three forms occur extensively in nature but not as constituents of natural fats. Lactic acid is the principal acid constituent of sour milk, and a normal constituent in the blood and muscle tissue of animals, and is widely distributed in nature in fruit juices. It has been identified in yeast fermentation, in corn steep liquor, sauerkraut, pickles, beer, buttermilk, and cheese.

Inactive or DL-lactic acid made by fermentation melts at 16.8°C .; sarcolactic (paralactic) or L(+)-lactic acids, the form occurring in blood, melts at 52.8°C . and has an optical rotation $[\alpha]_{5461}^{21} = -2.6$; its enantiomorph, D(−)-lactic acid, melts at 52.8°C . and has an optical rotation $[\alpha]_{5461}^{21} = 2.6$. The specific gravity of DL-lactic acid is 1.2060_4^{25} . It is very soluble in water and in water-miscible organic solvents such as ethanol and acetone.

Lactic acid is manufactured by fermentation of molasses, starch hydrolysates, or whey which produces essentially the inactive form. Several strains of *Lactobacillus* can be used for the fermentation, but it is preferable to use thermophilic bacteria of the *delbrueckii* type.

Lactic acid is marketed in several grades and concentrations, namely, (a) crude or technical in aqueous solutions of 22, 44, 66, and 80% concentration; (b) edible in 50 and 80% solution; (c) plastic in 50 and 80% solution; and (d) U.S.P. in 85% solution. It is also sold in the form of

TABLE 9
 Monohydroxyalkanoic Acids^a

Systematic name	M.p., ° C.	Methyl ester	
		M.p., ° C.	B.p., ° C./mm.
2-Hydroxydodecanoic	73-74	43 (ethyl ester)	
3-Hydroxydodecanoic	70-70.5		
4-Hydroxydodecanoic	62.5-63.5		
9-Hydroxydodecanoic	B.p. 156/1		
12-Hydroxydodecanoic	84-85	34-35	164-166/3
2-Methyl-2-hydroxyhendecanoic	46		
2-Hydroxytridecanoic	78		
4-Hydroxytridecanoic	66-66.5		
9-Hydroxytridecanoic	49-51		154-155/3
13-Hydroxytridecanoic	79-79.5	44	
2-Hydroxytetradecanoic	81.5-82		
3-Hydroxytetradecanoic	72-73		
11-Hydroxytetradecanoic	51		
14-Hydroxytetradecanoic	91-91.5	47	196-198/10
2-Hydroxypentadecanoic	84.5	48	
11-Hydroxypentadecanoic	63.5-64	29-32	166/2
15-Hydroxypentadecanoic	84.5-85.2	52-52.2	180-182/2
2-Hydroxyhexadecanoic	86-87	59-60	230-231/5
3-Hydroxyhexadecanoic	83-83.5		
11-Hydroxyhexadecanoic	68-69	40.5-41.5	183-186/3
16-Hydroxyhexadecanoic	95	55-55.5	194-196/2
2-Hydroxyheptadecanoic	89		
17-Hydroxyheptadecanoic	87.5-88	58.6-59	210/3
2-Methyl-16-hydroxyhexadecanoic	62-63		
2-Hydroxyoctadecanoic	91	66; 62-63	
3-Hydroxyoctadecanoic	89	51	
4-Hydroxyoctadecanoic	87	56-59	
5-Hydroxyoctadecanoic	82	52	
6-Hydroxyoctadecanoic	83	58	
7-Hydroxyoctadecanoic	78	51; 37.5 (ethyl ester)	
8-Hydroxyoctadecanoic	82	55.5	
9-Hydroxyoctadecanoic	75	50.5; 45-46	212-216/4
10-Hydroxyoctadecanoic	82	54	213-217/4
11-Hydroxyoctadecanoic	77	50	204-206/4
12-Hydroxyoctadecanoic (optically active)	82	58-59	202-204/4
12-Hydroxyoctadecanoic (<i>dl</i>)	79	53	185-189/2
13-Hydroxyoctadecanoic	77	53	
14-Hydroxyoctadecanoic	77 (γ); 80 (ε)	54.5	
15-Hydroxyoctadecanoic	75.5	59	
16-Hydroxyoctadecanoic	78.5	61	

TABLE 9 (Continued)

Systematic name	M.p., ° C.	Methyl ester	
		M.p., ° C.	B.p., ° C./mm.
17-Hydroxyoctadecanoic	76.5; 81	64	
18-Hydroxyoctadecanoic	99	62.5	
2-Hydroxynonadecanoic	83-84		
19-Hydroxynonadecanoic	91-91.5	65.5-66	
2-Hydroxyeicosanoic	91-92	62-64	
20-Hydroxyeicosanoic	97.4-97.8	68-68.5	
21-Hydroxyheneicosanoic	92.5-93	70-71	
2-Hydroxydocosanoic	98	70-71 (ethyl ester)	
13(14)-Hydroxydocosanoic	89-90	53	
2-Hydroxytetracosanoic	100		
22-Hydroxytetracosanoic	95-96		
2-Hydroxyhexacosanoic	86.5		
2-Hydroxytriacontanoic	97.5		
2-Hydroxytetratriacontanoic	109		

* Compiled by D. Swern (Chapter XIII) and originally published under the title, "Oxygenated Fatty Acids," *Progr. in Chem. Fats Lipids*, **3**, 214-241 (1955).

various salts (sodium and calcium) and esters (methyl, ethyl, and *n*-butyl). The acid is used in numerous products and processes, including the manufacture or preparation of food products, confections, and beverages; in the leather, textile, and plastics industries; in metal plating, printing and lithographing products, adhesives, insecticides and fungicides, etc.

Hydroxybutyric (Hydroxybutanoic) Acids, $C_4H_8O_2$. The three positional isomeric hydroxybutyric acids, namely, 2-hydroxybutanoic, $CH_3CH_2CHOHCOOH$; 3-hydroxybutanoic, $CH_3CHOHCH_2COOH$; and 4-hydroxybutanoic, $HOCH_2CH_2CH_2COOH$, are all well known but they are not important technically or as natural products.

The α -hydroxy acid can be prepared from *n*-butyric acid via the α -halogen acid or from propionaldehyde via the cyanohydrin. The L-2-hydroxybutanoic (m.p. 52.7-53.5° C.) was prepared by the method of anodic coupling by Horn and Pretorius (83) as already mentioned. The specific rotation in water was found to be $[\alpha]_D^{16} = 3.0^\circ$ and in $CHCl_3$ $[\alpha]_D^{16} + 6.4^\circ$. The β -hydroxy acid can be prepared (a) from acetoacetic ester by reduction and hydrolysis, (b) by the direct oxidation of butyric acid by hydrogen peroxide, and (c) by the partial oxidation of aldol. The levorotatory form of β -hydroxybutyric acid is found, together with acetoacetic

acid, in the urine of diabetics. The acid melts at 50° C. and distills at 130° C. and 12 mm. pressure.

The γ -hydroxy acid is extremely unstable and exists only in solution and in the form of salts and esters, because the free acid readily forms butyrolactone, its corresponding inner ester, through elimination of water.

The hydroxyisobutyric acids are also known. The esters of α -hydroxyisobutyric acid when treated with phosphorus pentachloride yield methylacrylic esters, $\text{CH}_2=\text{CCH}_3\text{COOR}$.

Hydroxyvaleric (Hydroxypentanoic) Acid, $\text{C}_5\text{H}_{10}\text{O}_3$. All four positional isomers of hydroxyvaleric acid are known. Each of the isomers can be synthesized by several methods. α -Hydroxyvaleric or 2-hydroxypentanoic acid can be prepared via the corresponding α -halogen or cyanohydrin; it is a hygroscopic solid melting at 34° C. β -Hydroxyvaleric or 3-hydroxypentanoic acid can best be prepared from butene-1-chlorohydrin; it is an unstable liquid which readily yields 3-pentenoic acid on heating. γ -Hydroxyvaleric or 4-hydroxypentanoic acid is best prepared by the reduction of commercially available levulinic acid (γ -ketovaleric acid) with sodium amalgam or by catalytic hydrogenation in the presence of a nickel catalyst. The acid exists per se only in solution. The free acid passes to the corresponding lactone which melts at -31° C., boils at 206-7° C. δ -Hydroxyvaleric or 5-hydroxypentanoic acid can be prepared by (a) the reduction of glutaric acid anhydride with aluminum amalgam, (b) the action of alcoholic sodium ethylate on 5-iodovaleric acid, and (c) via the malonic ester or acetoacetic ester synthesis using trimethylene bromohydrin. The acid is an oily liquid which readily forms δ -valerolactone. All four hydroxyvaleric acids are soluble in water, ethanol, and diethyl ether. Their chemical activity is markedly influenced by the position of the hydroxyl group.

The hydroxy derivatives of the isovaleric acids are also known. α -Hydroxyisovaleric acid on dehydration yields instead of a lactide, β,β -dimethylacrylic acid,



Hydroxycaproic (Hydroxyhexanoic) Acids, $\text{C}_6\text{H}_{12}\text{O}_3$. All of the isomeric hydroxycaproic acids have been prepared, but several of them are best known in the form of their corresponding lactones. α -Hydroxycaproic (2-hydroxyhexanoic) acid can be prepared by the action of nitrous acid on 2-aminohexanoic acid or by the debromination of 2-bromohexanoic acid. It is a colorless crystalline solid melting at 62° C. On distillation it yields valeraldehyde and a mixture of 2- and 3-hexenoic

acids. **Ls-2-Hydroxyhexanoic acid** (m.p. 61.0–61.6° C.) prepared by anodic coupling (83) had a specific rotation of $[\alpha]_D^{18} + 5.6$ in CHCl_3 .

β -Hydroxycaproic (3-hydroxyhexanoic) acid is obtained by debromination of 3-bromohexanoic acid in alkaline solution or by treatment of 2-hexenoic acid with sodium hydroxide solution. It is a colorless liquid at room temperature.

γ -Hydroxycaproic (4-hydroxyhexanoic) acid can be prepared by treatment of the corresponding bromide with sodium hydroxide solution or by treating 3-hexenoic (hydrosorbic) acid with concentrated sulfuric acid and hydrolyzing the addition product. Treatment of gluconic acid with phosphorus and hydrogen iodide has been reported to yield γ -hydroxycaproic acid. It readily forms a γ -lactone (m.p. $< -18^\circ \text{C}$., b.p. 220°C .).

δ -Hydroxycaproic (5-hydroxyhexanoic) acid is obtained by debrominating the corresponding bromohexanoic acid and by reduction of 5-ketohexanoic acid with sodium amalgam. It readily forms a lactone and is usually isolated as the barium salt.

ω -Hydroxycaproic (6-hydroxyhexanoic) acid is difficult to prepare in the free state since treatment of ω -bromocaproic acid with sodium ethylate leads to the formation of a polylactone.

Hydroxyheptanoic (Hydroxyenanthic) Acids, $\text{C}_7\text{H}_{14}\text{O}_3$. The α -substituted enanthic (2-hydroxyheptanoic) acid has been prepared by debromination of the corresponding 2-bromo acid. It melts at 65°C ., is difficultly soluble in cold water, yields caproic acid on oxidation with chromic acid, and hexanal when heated under proper conditions.

The γ -substituted acid (4-hydroxyheptanoic) is difficult to prepare because of its tendency to form the γ -lactone. Debromination of 4-bromoheptanoic acid with water yields a mixture of the hydroxy acid and γ -lactone. It has been prepared by treatment of 3-heptenoic acid with concentrated sulfuric acid and hydrolysis of the addition compound.

5-Hydroxyheptanoic (δ -hydroxyenanthic) acid can be prepared by debromination of the corresponding bromoheptanoic acid. It is a viscous liquid which exhibits ready lactone formation.

7-Hydroxyheptanoic (ω -hydroxyenanthic) acid has been prepared by partial reduction of pimelic acid, $\text{HOOC}(\text{CH}_2)_5\text{COOH}$. It is reported to be a syrupy liquid.

Hydroxycaprylic (Hydroxyoctanoic Acids, $\text{C}_8\text{H}_{16}\text{O}_3$. Three of the seven possible isomeric hydroxycaprylic acids have been prepared, namely, the α - and ω -hydroxycaprylic and 6-hydroxyoctanoic.

α -Hydroxycaprylic (2-hydroxyoctanoic) acid has been prepared by debromination of 2-bromoöctanoic acid with barium hydroxide and by

hydrolysis of 2-hydroxyoctanenitrile, $\text{CH}_3(\text{CH}_2)_5\text{CHOHCN}$, in the presence of hydrochloric acid. The acid melts at 69.5°C ., is very soluble in diethyl ether and ethanol, but slightly soluble in cold water. The L-2-hydroxyoctanoic acid (m.p. $70.2\text{--}70.6^\circ \text{C}$.) prepared by anodic coupling (83) has a specific rotation $[\alpha]_{\text{D}}^{19} + 1.5^\circ$ in chloroform.

ω -Hydroxyeaprylic (8-hydroxyoctanoic) acid has been prepared by partial reduction of potassium methyl suberate, $\text{KOOC}(\text{CH}_2)_6\text{COOCH}_3$, with sodium in ethanol solution. It melts at 58°C . and yields a dimeric lactone on heating with benzenesulfonic acid.

6-Hydroxyoctanoic acid has been obtained by the reduction of 6-keto-octanoic acid with zinc and potassium hydroxide.

Hydroxypelargonic (Hydroxynonanoic) Acids, $\text{C}_9\text{H}_{18}\text{O}_3$. Four of the eight position isomers of hydroxypelargonic acid have been prepared, namely, α -, β -, and ω -hydroxypelargonic, and 7-hydroxynonanoic.

α -Hydroxypelargonic (2-hydroxynonanoic) acid has been prepared by the debromination of 2-bromononanoic acid with potassium hydroxide. It melts at 70°C . and yields octanal and the corresponding lactide when heated.

β -Hydroxypelargonic (3-hydroxynonanoic) acid, heptanoic acid, and 1,2,4-decanetriol are formed by the oxidation of hexyl allyl carbinol. The reported melting point of the acid is $48\text{--}51^\circ \text{C}$.

ω -Hydroxypelargonic (9-hydroxynonanoic) acid has been obtained in 31.5% yield by the partial reduction of potassium methyl azelate with sodium in ethanol. Reduction of dimethyl azelate, $\text{CH}_3\text{OOC}(\text{CH}_2)_7\text{COOH}$, yields 8% of the hydroxy acid and 73% of the corresponding glycol. Conversion of the latter to the monobromohydrin, $\text{CH}_2\text{Br}(\text{CH}_2)_7\text{CH}_2\text{OH}$, and oxidation to the corresponding acid, $\text{CH}_2\text{Br}(\text{CH}_2)_7\text{CH}_2\text{COOH}$, followed by treatment with potassium ethylate and hydrolysis of the resulting product yields the free acid and its etholide. The acid melts at $51\text{--}51.5^\circ \text{C}$. and its lactone at $24\text{--}26.5^\circ \text{C}$.

7-Hydroxynonanoic acid can be prepared by reduction of the corresponding keto acid with zinc and potassium hydroxide.

Hydroxycapric (Hydroxydecanoic) Acids, $\text{C}_{10}\text{H}_{20}\text{O}_3$. α -Hydroxycapric (2-hydroxydecanoic) acid can be obtained by debromination of 2-bromodecanoic acid with potassium hydroxide. It melts at 70.5°C . and decomposes on heating with formation of nonanal. L-2-Hydroxydecanoic acid (m.p. $77.6\text{--}78^\circ \text{C}$.) prepared by anodic coupling (83) has a specific rotation in CH_3Cl $[\alpha]_{\text{D}}^{24} + 5.3^\circ$

The optically active (—)3-hydroxydecanoic acid has been isolated by Bergström *et al.* (85) from *Pseudomonas pyocyanea* fat.

γ -Hydroxycapric (4-hydroxydecanoic) acid and the corresponding 4-hexylbutyl lactone, are obtained by debromination of 4-bromodecanoic acid with sodium hydroxide. The acid has also been obtained by distillation of hexylparaconic acid,



and by the action of fuming hydrochloric acid on the oxime of 12-hydroxy-9-ketostearic acid.

ω -Hydroxycapric (10-hydroxydecanoic) acid is obtained on partial reduction of various derivatives of sebacic acid, $\text{HOOC}(\text{CH}_2)_8\text{COOH}$. The free acid readily undergoes lactonization with the formation of a mono- as well as a dimeric and trimeric lactone and it also undergoes etholide formation yielding a mono- and dietholide. The monolactone melts at 4–5° C. 10-Hydroxydecanoic acid has been reported to yield polymers having molecular weights between 1000 and 9000.

Hydroxyhendecanoic (Hydroxyundecanoic) Acids, $\text{C}_{11}\text{H}_{22}\text{O}_3$. The best known of the ten isomeric hydroxyundecanoic acids are the α -hydroxy- and ω -hydroxy-substituted acids. α -Hydroxyundecanoic (2-hydroxyhendecanoic) acid is readily obtained by debromination of 2-bromohendecanoic acid with potassium hydroxide. It melts at 69° C. and yields decanal on distillation.

ω -Hydroxyundecanoic (11-hydroxyhendecanoic) acid has been prepared by debromination of 11-bromohendecanoic acid with silver oxide in alkaline solution, by hydrolysis of 11-hydroxydecanenitrile, and by heating the condensation product of 9-bromo-1-nonanol with dimethyl sodiomalonate. The free acid is only slightly soluble in water (0.04 g./100 g. water at 20° C.) but is easily soluble in diethyl ether and ethanol. It forms a mono- and dimeric lactone. The latter melts at 71.5–72° C.

Hydroxylauric (Hydroxydodecanoic) Acids, $\text{C}_{12}\text{H}_{24}\text{O}_3$. α -Hydroxylauric (2-hydroxydodecanoic) acid has been synthesized and also isolated from natural sources. Horn, Hougén, and von Rudloff (86) found the acidic fraction of wool grease extracted from Merino fleece to contain 30% of hydroxylated fatty acids including 0.6% n - α -hydroxylauric, 3.8% n - α -hydroxymyristic, 18.8% n - α -hydroxypalmitic, and 4.6% n - α -hydroxystearic; also an undetermined amount of 16-methyl-2-hydroxyheptanoic acid. The alpha acids were optically active (87) and were later synthesized from an optically active half-ester of (–)-malic acid by anodic coupling with aliphatic acids (83). Inactive α -hydroxylauric acid is

easily prepared by the action of aqueous potassium hydroxide on 2-bromododecanoic acid. It melts at 73–74° C. and yields decanal on distillation.

γ -Hydroxylauric (4-hydroxydodecanoic) acid has been prepared by saponification of its lactone. The acid melts at 62.5–63.5° C.

ω -Hydroxylauric (12-hydroxydodecanoic) acid, also called sabinic acid, occurs in the leaf wax of the savin juniper (*Juniperus sabina*) in the form of its etholide, $\text{HOCH}_2(\text{CH}_2)_{10}\text{COOCH}_2(\text{CH}_2)_{10}\text{COOH}$ (88). The free acid has been synthesized (89) by condensation of 10-bromo-1-decanol with dimethyl malonate in the presence of sodium, and also by oxidation of 12-tridecenyl acetate. The acid melts at 84° C. and is readily soluble in ethanol.

The 3-hydroxy- and 9-hydroxydecanoic acids are also known (see Table 9).

Hydroxytridecanoic Acids, $\text{C}_{13}\text{H}_{26}\text{O}_3$. Several hydroxytridecanoic acids have been synthesized, including the 2-hydroxy, 4-hydroxy, and 13-hydroxy acids. 2-Hydroxytridecanoic acid has been prepared via the corresponding bromo acid. It melts at 78° C. and is readily soluble in ethanol and diethyl ether but is insoluble in petroleum naphtha and benzene.

4-Hydroxytridecanoic acid has been obtained by saponification of its γ -lactone. It melts at 66–66.5° C.

13-Hydroxytridecanoic acid has been prepared by the partial reduction of the dimethyl ester of tridecanoic acid, $\text{CH}_3\text{COO}(\text{CH}_2)_{11}\text{COOCH}_3$, with sodium and ethanol. It melts at 79–79.5° C. and its methyl ester at 44° C. It forms a monolactone melting at 20–21° C. and a dimeric lactone at 80–81° C.

Hydroxymyristic (Hydroxytetradecanoic) Acids, $\text{C}_{14}\text{H}_{28}\text{O}_3$. Several hydroxymyristic acids have been isolated from natural sources. Müller (90) as long ago as 1881 isolated a hydroxymyristic acid from *Angelica archangelica* oil. The acid melted at 51° C. but its exact constitution was not established. An optically active 2-hydroxytetradecanoic acid has been isolated from beeswax (87) and its presence in wool fat was demonstrated by Weitkamp (20). The acid obtained from wool fat melted at 88.5° C. but its rotation was not determined. Horn and Pretorius (83) assigned it and the other hydroxy acids isolated from the same source a D_s -configuration.

α -Hydroxymyristic (2-hydroxytetradecanoic) acid has been prepared by debromination of the corresponding 2-bromomyristic acid. The acid melted at 51–51.5° C. and was readily soluble in diethyl ether, ethanol, and acetone.

ω -Hydroxymyristic (14-hydroxytetradecanoic) acid has been prepared by the partial reduction of the methyl ester of tetradecanedioic acid, $\text{CH}_3\text{COO}(\text{CH}_2)_{12}\text{COOCH}_3$; by conversion of 13-bromo-1-tridecanol to the corresponding 13-cyano-1-tridecanol and hydrolysis of the nitrile to the corresponding acid; and by condensation of dimethyl sodiomalonate with 12-bromo-1-dodecanol. The acid melts at $54\text{--}54.5^\circ\text{C}$. and forms a monomeric lactone (b.p. $106\text{--}109^\circ\text{C}$. at 2 mm. pressure) and a dimeric lactone melting at $106\text{--}107^\circ\text{C}$.

Hydroxypentadecanoic Acids, $\text{C}_{15}\text{H}_{30}\text{O}_3$. Various hydroxypentadecanoic acids have been reported to occur in nature or have been synthesized. 2-Hydroxypentadecanoic acid (m.p. 84.5°C . has been prepared by the action of sodium hydroxide on 2-bromodecanoic acid. It is readily soluble in ethanol but is difficultly soluble in cold benzene. 11-Hydroxypentadecanoic acid (m.p. $63.5\text{--}64^\circ\text{C}$.) has been synthesized by the reaction of butylmagnesium bromide and methyl 11-aldohendecanoate. 15-Hydroxypentadecanoic acid was prepared by Chuit and Hausser (89) by the partial reduction of the dimethyl ester of pentadecanedioic acid and also by the malonic acid method from 13-bromo-1-tridecanol.

An optically active hydroxypentadecanoic acid (convolvulinic acid) has been reported to be present in convolvulin resin isolated from the roots of *Convolvulus scammonia* L. (91). The acid on reduction, conversion to the oxime, and rearrangement of the oxime gave a pentadecanoic acid. On the basis of these reactions Asahina and Akasu (92) concluded that the natural acid was 11-hydroxypentadecanoic acid. However, the properties of the natural and the corresponding synthetic acid are sufficiently different to render the identification dubious.

Another hydroxypentadecanoic acid has been reported to be present in angelica oil. On oxidation this acid gave pentadecanedioic acid, $\text{HOOC}(\text{CH}_2)_{13}\text{COOH}$ and hence the original acid was presumed to be 15-hydroxypentadecanoic acid.

A 2-hydroxypentadecanoic acid was prepared from ustilic acid B by Lemieux (93) and was subsequently assigned a D_x-configuration by Horn and Pretorius (83). The hydroxy acid melted at $89.5\text{--}90^\circ\text{C}$. and had a rotation $[\alpha]_D -0.8^\circ$ in ethanol.

Hydroxypalmitic (Hydroxyhexadecanoic) Acids, $\text{C}_{16}\text{H}_{32}\text{O}_3$. Several hydroxypalmitic acids have been isolated from natural sources and a few of them have been synthesized. Juniperic or 16-hydroxyhexanoic acid appears to be the first isomer of this group to be isolated from natural sources. It was obtained by Bougault and Bourdier (94) by hydrolysis of the etholides of coniferous waxes (*Juniperus sabina*, *Picea*

abies, and *Thuja occidentalis*) and subsequently was shown by Bougault (95) to be ω -hydroxypalmitic acid. The acid melted at 95° C., but after heating for a short time the melting point decreased to 83° C., probably the result of etholide formation. The acid has been synthesized by the partial reduction of dimethyl thapsate (dimethyl hexadecanedioic acid), $\text{CH}_3\text{COO}(\text{CH}_2)_{14}\text{COOCH}_3$, and by the oxidation of the monoacetate of 1,16-hexadecanediol (89). The dietholide prepared by heating the free acid to 125° C. melts at 87.5–88.0° C.

Jalapinolic or 11-hydroxypalmitic acid was isolated by Power and Rogerson (96) from jalop or Mexican scammony root wax (*Ipomea orizabensis*). The acid was later synthesized by Davies and Adams (97) by the action of *n*-amylmagnesium bromide on methyl 11-aldodecanoate. This acid melted at 68–69° C.

A hydroxypalmitic acid has been reported by various authors (98) to be present in beeswax. It is presumed to be the 14-hydroxy isomer but its identity has not been unequivocally established.

Optically active α -hydroxypalmitic acid was isolated from wool fat by Weitkamp (20) and by Horn *et al.* (86). The acid melted at 93.6° C. which differentiated it from the previously known inactive forms. The optically active and racemic forms of 2-hydroxyhexadecanoic (α -hydroxypalmitic) acid have been prepared synthetically. Inactive forms have been obtained by the action of potassium hydroxide on 2-bromo- and 2-iodopalmitic acid. The acid is reported to melt at 86.5–87° C. Horn *et al.* (83,86) prepared DL-2-hydroxy- (m.p. 85.8–86.6° C.), L_s-2-hydroxy- (m.p. 93.3–93.6° C.) and D_s-2-hydroxyhexadecanoic acids. The L_s- and D_s-forms had specific rotations as follows: $[\alpha]_D^{26} + 2.7^\circ$ in chloroform and $[\alpha]_D^{22} + 1^\circ$ in 50% ethanol, respectively. The acid isolated from wool wax was assigned the D_s-configuration.

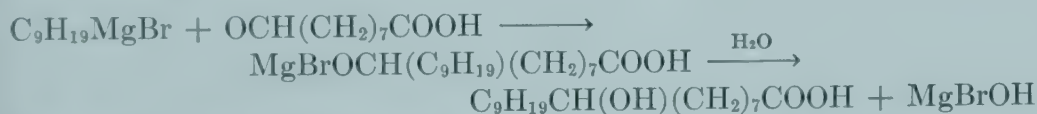
Buiolic or 11-hydroxyhexadecanoic acid has been isolated from shellac. It was obtained as a crystalline compound melting at 55° C. (98a).

Hydroxyheptadecanoic Acids, C₁₇H₃₄O₃. No hydroxyheptadecanoic acids appear to have been isolated from natural sources, and only two, the alpha and omega acids, have been synthesized. 2-Hydroxyheptadecanoic acid has been prepared by the action of potassium hydroxide on 2-bromoheptadecanoic acid. It melts at 89° C. 17-Hydroxyheptadecanoic acid has been prepared by the partial reduction of the dimethyl ester of heptadecanedioic acid. It melts at 87.5–88.0° C. It forms a monomeric and dimeric lactone when heated in the presence of benzenesulfonic acid.

Hydroxystearic (Hydroxyoctadecanoic) Acids, $C_{18}H_{36}O_3$. Several hydroxystearic acids have been reported to be present in various natural or altered fatty substances (99–102), including wool fat (103), Druschky rose wax (104), and autoxidized unsaturated fatty acids (105). For the most part these acids have remained unidentified because at the time of isolation no reference compounds were available for comparison with the natural product. Since then all of the possible positionally isomeric hydroxyoctadecanoic acids have been synthesized in their DL-forms and in a few cases in optically active form.

Some of the isomers have been prepared by several workers and by different methods. The alpha isomer has been prepared by the classical reaction of potassium hydroxide on 2-bromo- or 2-iodostearic acid, and the omega isomer by the equally classical method of partial reduction of the dimethyl ester of the corresponding dioic acid, $CH_3COO(CH_2)_{16}COOCH_3$.

The 9-, 10-, 11-, 12-, and 13-hydroxystearic acids were synthesized by Tomecko and Adams (106) by the Grignard method. For example, 9-hydroxystearic acid was prepared by reacting 9-alidonanoic acid with nonylmagnesium bromide as follows:



The other acids were prepared in the same manner using the appropriate reactants.

10-Hydroxystearic acid has been prepared by (a) hydrolysis of the sulfuric acid addition products of oleic and elaidic acids, (b) the reaction of silver oxide on 10-iodostearic acid, and (c) the catalytic hydrogenation of *cis*- and *trans*-epoxystearic acid with palladium-carbon catalyst (107). Reduction of both the *cis*- and *trans*-forms gave the same 10-hydroxystearic acid. According to Roe *et al.* (108), sulfation of oleic acid and subsequent hydrolysis of the addition product yields a mixture of 9-hydroxy- and 10-hydroxystearic acids together with other hydroxystearic acids resulting from a shift of the substituent group along the carbon chain. The composition of the mixed hydroxystearic acids depends on the conditions of sulfation. Undoubtedly an equally heterogeneous mixture of hydroxystearic acids is obtained when the same reaction is applied to elaidic acid.

12-Hydroxystearic acid can be obtained by the reaction of zinc and hydrochloric acid on the hydrogen bromide addition product of ricinoleic

acid and by hydrogenation of ricinoleic acid or its methyl ester. According to Walden (109), hydrogenation of the ester in the presence of a platinum catalyst leads to an optically active hydroxystearic acid.

In 1952 Bergström *et al.* (110) reported the synthesis of the entire series of seventeen DL-forms of monohydroxyoctadecanoic acids and their methyl esters together with thermal and x-ray data for each product (see Chapter IV). Except for the 2-hydroxy- and 18-hydroxystearic acids, which were prepared by conventional methods, all of the acids were prepared via the methyl esters obtained by high pressure hydrogenation over Raney nickel of the methyl esters of the corresponding keto acids.

Gupta and Aggarwal (110a) prepared 18-hydroxystearic acid by hydrogenation of kamolenic acid obtained from kamela seed oil. The hydroxy acid, which was obtained in 90% yield, melted at 95–97° C.

Hydroxynonadecanoic Acid, $C_{19}H_{38}O_3$. Of the eighteen possible position isomers of hydroxynonadecanoic acid only the α -hydroxy and ω -hydroxy acids have been prepared. Chuit and Hausser (89) obtained 19-hydroxynonadecanoic acid in small yield by the partial reduction of the dimethyl ester of nonadecanedioic acid. The free acid melted at 91–91.5°, the acetyl derivative at 70.0–70.2°, and the methyl ester at 65.6–66.0° C. The 2-hydroxy acid was prepared by the treatment of the corresponding bromo acid with potassium hydroxide.

Hydroxyeicosanoic Acids, $C_{20}H_{40}O_3$. 2-Hydroxyeicosanoic (2-hydroxyarachidic) acid, melting at 91–92° C., has been prepared by heating 2-bromoarachidic acid with alcoholic sodium hydroxide. The terminal substituted acid was included in the series ω -hydroxy saturated acids prepared by Chuit and Hausser (89) by the partial reduction of dimethyl esters of the corresponding dicarboxylic acids. The free acid obtained in this manner from the diester of eicosanedioic acid in small yield melted at 97.4–97.8°, the methyl ester at 68–68.5°, and the acetyl derivative at 77° C.

Hydroxyheneicosanoic Acid, $C_{21}H_{42}O_3$. Only the 21-hydroxyheneicosanoic acid appears to have been prepared. It was obtained by Chuit and Hausser (89) by the partial reduction of the dimethyl ester of heneicosanedioic acid. The free acid melted at 92.5–93.0° and the acetyl derivative at 73.8–74.2° C.

Hydroxydocosanoic (Hydroxybehenic) Acids, $C_{22}H_{44}O_3$. Phellonic acid is the principal hydroxy fatty acid obtained by the saponification of the outer bark of the cork oak (*Quercus suber*), a tree indigenous to the Western Mediterranean. The acid comprises 50–72% of the total acids obtained from cork and 12–27% of the cork (111). Zetzsche and Son-

deregger (112) assigned the formula $C_{22}H_{44}O_3$ to the acid and believed that the hydroxyl group occupied a position alpha to the carboxyl. Subsequently, Drake *et al* (113) concluded that the acid was 22-hydroxytetracosanoic, but later workers (114) have shown that phellonic acid is ω -hydroxybehenic. The identification made by Ribas *et al.* (114) was based on the urea adducts of phellonic acid and its acetylation product, elementary analysis of the methyl ester, neutralization equivalent, potassium salt, etc.

2-Hydroxydocosanoic acid has been prepared by the action of aqueous potassium hydroxide on 2-bromobehenic acid.

Hydroxytetracosanoic (Hydroxylignoceric) Acids, $C_{24}H_{48}O_3$. Four closely related C_{24} -acids have been isolated from the hydrolysates of brain cerebroside, namely, lignoceric, $CH_3(CH_2)_{22}COOH$; α -hydroxylignoceric or cerebronic; nervonic or 15-tetracosenoic; and α -hydroxynervonic. The principal hydroxy saturated fatty acid isolated from the brain is cerebronic, which has at various times been assumed to be 2-hydroxypentacosanoic (115), 2-hydroxytetradecanoic (116), and a mixture of 2-hydroxydocosanoic, 2-hydroxytetracosanoic, and 2-hydroxyhexacosanoic acids (117) in which the 2-hydroxytetracosanoic acid predominated. According to Chibnall *et al.* (117), cerebronic acid is a mixture of 85% α -hydroxytetracosanoic and 15% α -hydroxyhexacosanoic acids. However, Müller (118) synthesized DL-2-hydroxytetracosanoic acid by the action of potassium hydroxide on 2-bromotetracosanoic acid, separated the dextro acid by means of its strychnine salt, and found it to be identical with the naturally occurring cerebronic acid. The acid melted at 99.5–100.5° C. and had a specific rotation, $[\alpha]_D^{25} + 3.7^\circ$ in pyridine.

Higher Molecular Weight Monohydroxyalkanoic Acids. Several higher molecular weight acids of doubtful authenticity have been prepared from corresponding natural acids. For example, Marie (119) in 1896 prepared 2-hydroxycerotic ($C_{26}H_{52}O_3$) and 2-hydroxymelissic ($C_{30}H_{60}O_3$) acids by the action of alcoholic potassium hydroxide on the 2-bromo derivatives of cerotic and melissic acids. The hydroxy acids were reported to melt at 86.5° and 97.5° C., respectively. Since most of the high molecular weight acids isolated at that time were mixtures of several acids of mean molecular weight corresponding to the described acid it may be assumed that the hydroxy acids prepared from them were likewise mixtures of several acids.

As mentioned above Chibnall (117) found cerebronic acid isolated from brain cerebroside to consist of a mixture of 2-hydroxytetracosanoic and 2-hydroxyhexacosanoic acids.

(d) *Polyhydroxyalkanoic Acids*

Compared with the number of known natural and synthetic mono-hydroxyalkanoic acids, only a few polyhydroxy saturated acids are known. Of these even fewer have been found as constituents of natural fats. Certain polyhydroxy acids, such as dihydroxyacetic, $(\text{HO})_2\text{-CHCOOH}$, in reality the hydrated form of the aldehyde acid, glyoxylic, OCHCOOH ; glyceric acid, $\text{HOCH}_2\text{CHOHCOOH}$; α,γ -dihydroxybutyric acid, $\text{HOCH}_2\text{CH}_2\text{CHOHCOOH}$; and the various sugar acids (pentonic, hexonic, etc.) are of interest to the organic and biological chemist but are outside the scope of the present work. With few exceptions our knowledge of the high molecular weight, polyhydroxy fatty acids has been obtained from studies of the oxidation of unsaturated fatty acids.

The hydroxyl groups of di- or other polyhydroxy acids may be attached to adjacent or nonadjacent carbon atoms. Acids of the former type (α -glycol or vicinal) are the better known. Since each dihydroxy acid, with the exception of those having a terminal hydroxyl, contains two asymmetric carbon atoms, there are four optical isomers possible and two racemic mixtures.

The vicinal dihydroxy fatty acids and tetra- and hexahydroxy fatty acids are formed by oxidation at the double bonds of unsaturated acids with potassium hydroxide or osmium tetroxide under mild conditions. *cis*-Unsaturated acids yield a mixture of the higher-melting *DL-erythro* (or *cis*)-dihydroxy fatty acids melting from 115° to 135° C., while the *trans*-acids yield *DL-threo* (or *trans*)-dihydroxy acids melting from 70° to 100° C.

Polyhydroxy fatty acids are soluble in hot water and in ethanol, less soluble in ethyl ether, and insoluble in petroleum naphtha. By splitting two molecules of water from vicinal dihydroxy acids, conjugated double-bond fatty acids can be prepared. Such acids have applications in the drying oil industry. Methods of preparation and reactions of the polyhydroxy fatty acids, together with the properties and reactions of the end products are discussed in detail in Chapter XIII.

The principal polyhydroxyalkanoic acids isolated from natural sources are assembled in Table 10.

Dihydroxytetradecanoic (Ipurolic) Acid, $\text{C}_{14}\text{H}_{28}\text{O}_4$. Ipurolic or 3,11-dihydroxymyristic acid was isolated from the seed fat of *Ipomea purpurea* (South African morning glory) by Power and Rogerson (120) and was later obtained by Asahina *et al.* (121) by hydrolysis of pharbitic acid from *Pharbitis nil* Choisy (Japanese morning glory) who also confirmed its

TABLE 10
Polyhydroxyalkanoic Acids from Natural Sources

Systematic name	Common name	Molecular formula	Formula weight	Neutralization value	M.p., ° C.	Source
3,11-Dihydroxytetradecanoic	Ipurolic ^a	C ₁₄ H ₂₈ O ₄	260.36	215.48		<i>Ipomea purpurea</i>
2,15-Dihydroxypentadecanoic	Dihydroxypentadecylic	C ₁₅ H ₃₀ O ₄	274.39	204.47	102	Ustilic acid B
15,16-Dihydroxyhexadecanoic	Dihydroxypalmitic	C ₁₆ H ₃₂ O ₄	288.42	194.52	112	
9,10-Dihydroxyoctadecanoic	Dihydroxystearic	C ₁₈ H ₃₆ O ₄	316.47	177.28	141	Castor oil
9,10-Dihydroxyoctadecanoic	Dihydroxystearic	C ₁₈ H ₃₆ O ₄	316.47	177.28	90	Soils and straw
9,10-Dihydroxyoctadecanoic	Dihydroxyarachidic	C ₂₀ H ₄₀ O ₄	344.52	162.85	130	Hare's-ear mustard-seed oil
11,12-Dihydroxyicosanoic	Lanocerinic ^b	C ₃₀ H ₆₀ O ₄	484.78	115.73	104	Wool fat
Dihydroxytriacontanoic	Ustilic ^c	C ₃₁ H ₆₂ O ₅	304.42	184.30	140	
2,15,16-Trihydroxyhexadecanoic	Trihydroxypalmitic	C ₁₆ H ₃₂ O ₅	304.42	184.30	100	Shellac
8,9,16-Trihydroxyhexadecanoic	Aleuritic ^c	C ₁₆ H ₃₂ O ₅	304.42	184.30	100	Shellac
9,10,16-Trihydroxyhexadecanoic	Trihydroxypalmitic	C ₁₆ H ₃₂ O ₅	304.42	184.30	100	Shellac
11,12,15-Trihydroxyhexadecanoic	Kerrollic ^d	C ₁₆ H ₃₂ O ₆	320.42	175.10	132	Shellac
Tetrahydroxyhexadecanoic						

^a Also dihydroxymyristic.

^b Also dihydroxymelissic.

^c Also trihydroxypalmitic.

^d Also tetrahydroxypalmitic.

structure by partial dehydration to 11-hydroxy-2-tetradecenoic acid and hydrogenation to 11-hydroxytetradecanoic acid.

Dihydroxypentadecanoic Acid, $C_{15}H_{30}O_4$. Lemieux (93) prepared from ustilic acid B ($2_D, 15_D, 16$ -trihydroxypalmitic acid) an optically active acid melting at $102-103^\circ C$. which was identified as $2_D, 15$ -dihydroxypentadecanoic acid.

Dihydroxyhexadecanoic (Ustilic) Acid, $C_{16}H_{32}O_4$. A dihydroxypalmitic acid designated by Lemieux (93) as ustilic acid A was shown by him to be $15_D, 16$ -dihydroxyhexadecanoic acid. The acid melts at $112-113^\circ C$. and has an optical rotation $[\alpha]_D -8^\circ$ in methanol. Its hydrazide melts at $140.5-141.5^\circ C$.

Dihydroxyoctadecanoic Acid, $C_{18}H_{36}O_4$. 9,10-Dihydroxystearic acid was isolated from castor oil (*Ricinis communis* L.) in 1925 by Eibner and Münzing (122) and since then by a number of others (123) in amounts varying from 0.6 to 2.4%. It has also been reported to be present in the oil of lycopodium (124). The natural acid is optically active and melts at $141^\circ C$. Another dihydroxy stearic acid designated as *DL-threo*-9,10-dihydroxyoctadecanoic, melting point $90^\circ C$., has been found in soils and straw.

In addition to the natural dihydroxystearic acids discussed above at least eight such acids have been synthesized in the form of their low-melting and high-melting racemic mixtures. The preparation and properties of these acids are discussed in Chapter XIII.

Dihydroxyeicosanoic Acid, $C_{20}H_{40}O_4$. 11,12-Dihydroxyarachidic has been isolated from hare's-ear mustard-seed oil by Hopkins (125). The acid melted at $130^\circ C$.

Dihydroxytriacontanoic (Lanoceric) Acid, $C_{30}H_{60}O_4$. In 1896 Darmstaedter and Lifschütz (126) reported the isolation of a dihydroxy acid from wool fat which melted at $104-105^\circ C$. and corresponded to the empirical formula given above. They named the acid lanoceric acid. The same acid was isolated again by Abraham and Hilditch (127) in 1935 from the same source.

Trihydroxyhexadecanoic Acids, $C_{16}H_{32}O_5$. Several trihydroxyhexadecanoic (trihydroxypalmitic) acids have been reported to be components of shellac, a protective resinous incrustation secreted by the insect *Laccifer lacca* Kerr, which is indigenous to southeast Asia and contiguous islands. The various polyhydroxy carboxylic acids appear to be present in shellac in the form of mixtures of several inter-esters. The most important and best known of the shellac acids is aleuritic or erythro-9,10,16-trihydroxyhexadecanoic acid. It is obtained in relatively constant yields

of about 43% by saponifying dewaxed shellac with 20% sodium hydroxide solution, treating the saponification mixture with kieselguhr, and separating the crystalline sodium aleuritate by filtration.

The length of the carbon chain of alueritic acid was established by reducing it to palmitic acid with hydrogen iodide, and the positions of the hydroxy groups were determined by oxidation with potassium permanganate, lead tetraacetate, and by other reactions. Oxidation of aleuritic acid with potassium permanganate yields, depending on the reaction conditions, azelaic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOH}$ and 7-hydroxyenanthic (7-hydroxyheptanoic) acid; or azelaic and pimelic acid, $\text{HOOC}(\text{CH}_2)_5\text{COOH}$. Oxidation with lead tetraacetate yields azelaic hemialdehyde, $\text{HOOC}(\text{CH}_2)_5\text{CHO}$. Splitting the acid with dilute alkali yields azelaic acid and 7-hydroxyheptanoic acid, $\text{HOCH}_2(\text{CH}_2)_5\text{COOH}$. The determination of the structure of aleuritic acid is due largely to the work of Nagel *et al.* (127a) and of Mitter *et al.* (127b) who studied the products of oxidation, reduction, and derivatives of this acid, and also synthesized it by various methods.

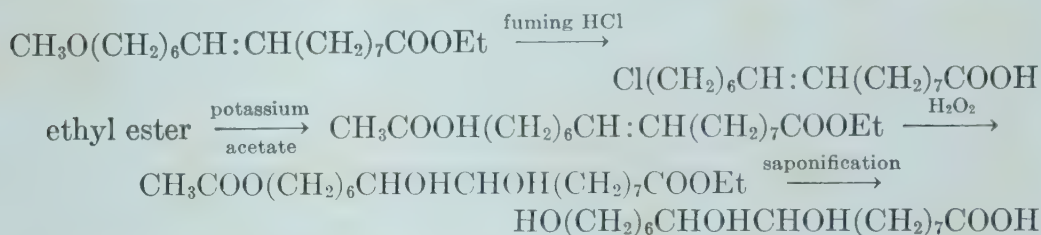
Aleuritic acid melts at $100\text{--}101^\circ\text{C}$., although melting points as high as 104° have been reported. It is optically inactive although it contains two asymmetric carbon atoms. It may be assumed to be either DL-erythro (*dl-cis* or (β)) or DL-threo (*dl-trans* or α) but present evidence indicates that it should be assigned an erythro configuration, that is, a configuration corresponding to the sugar erythrose.

Several other trihydroxypalmitic acids have been reported to be present in shellac. Endemann (127c) isolated an acid melting at $100\text{--}101^\circ\text{C}$. which he believed to be 11,12,15-trihydroxypalmitic acid and Rittler (127d) reported the isolation of another acid, also melting at 101°C ., whose products of oxidation indicated that it was 8,9,16-trihydroxypalmitic acid. Weinberger and Gardner (127e) obtained an isomeric acid melting at $89\text{--}90^\circ\text{C}$. and others have reported the isolation of one melting at $97\text{--}97.5^\circ\text{C}$.

A number of trihydroxypalmitic acids have been prepared synthetically. Collaud (127f) synthesized 6,7,16-trihydroxypalmitic acid melting at $100\text{--}101^\circ\text{C}$. and Mitter *et al.* synthesized 8,9,16- and 9,10,16-trihydroxypalmitic acids. The last-mentioned acid melted at 125°C . compared with $100\text{--}101^\circ\text{C}$. for the natural acid. The same acid apparently was prepared by Hunsdiecker (127g) and by Baudert (127h). These acids may be DL-threo-9,10,16-trihydroxypalmitic acid, and if this is correct, it may be that natural aleuritic acid is a racemic erythro product and should be capable of resolution into two optical isomers.

9,10,16-Trihydroxypalmitic acid (m.p. 125° C.) was synthesized by Mitter, Sen-Gupta, and Bose (127b) starting with 16-methoxy-9-hexadecenoic acid which had been synthesized previously by Mitter and Mukherjee (127b). The ethyl ester, $\text{CH}_3\text{O}(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOEt}$, was converted to 16-chloro-9-hexadecenoic acid by treatment with fuming hydrochloric acid. The chlorinated ester was acetylated with potassium acetate and the acetyl derivative oxidized with hydrogen peroxide to 16-acetoxy-9,10-dihydroxypalmitic acid, which was saponified to give 9,10,16-trihydroxypalmitic acid. The synthetic acid (m.p. 125° C.), when mixed with natural aleuritic acid (m.p. 100–101° C.) melted at 101° C.

The reactions involved in the synthesis may be represented as follows:



A trihydroxypalmitic acid designated as ustilic acid B was shown by Lemieux (93) to be 2_D,15_D,16-trihydroxyhexadecanoic acid. It melts at 140–141° C. and has an optical rotation $[\alpha]_D -10^\circ$ in methanol. Its hydrazide melts at 164–165° C.

Tetrahydroxyhexadecanoic (Kerrollic) Acid, $\text{C}_{16}\text{H}_{32}\text{O}_6$. A tetrahydroxypalmitic acid which has been designated kerrollic acid, melting at 132° C., has been obtained from shellac in the form of a crystalline powder from the fraction of acids forming water-soluble lead salts. The acid is not very stable in the presence of heat.

Synthetic Polyhydroxy Acids. An appreciable number of dihydroxy and other polyhydroxy fatty acids have been prepared by hydroxylation of the more common mono- and polyunsaturated fatty acids. The synthesis, reactions, and properties of these acids are discussed in Chapter XIII.

(e) Ketoalkanoic Acids

Few ketoalkanoic acids have been isolated from natural sources and none is of commercial importance per se. The 3-ketoalkanoic acids are intermediate products of fatty acid catabolism and the resulting methyl ketones, especially those derived from the lower molecular weight fatty acids, contribute to the rancidity of certain types of fats, e. g., coconut

and palm kernel oils. Several of the lower molecular weight ketoalkanoic acids are of biological significance or are important intermediates in organic syntheses, e. g., pyruvic or ketopropionic acid, $\text{CH}_3\text{COCO}_2\text{H}$; acetoacetic or β -ketobutyric acid, $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$; levulinic or γ -ketovaleric acid, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$, etc.

Small amounts of ketoalkanoic acids are reported to be formed by the action of certain microorganisms involved in the production of so-called ketonic rancidity. Lactarinic (6-ketostearic) acid was isolated from the mushroom fungus, *Lactarius refus*, in 1911 by Bougault and Charaux (128) and by Zellner (129) in 1920. The former obtained the acid in a yield of 2 to 3% by extraction of the dried fungus with hot ethanol compared to a yield of 1% reported by Zellner. The wax of the white pine (*Pinus strobus* L.) has been reported to contain an ester of 17-ketohexatriacontanol and 11-ketotriacontanoic (ketomelissic) acid, $\text{C}_{30}\text{H}_{58}\text{O}_3$. Chibnall *et al.* (130) have suggested that the higher molecular weight keto fatty acids, formed as condensation products of normal fatty acids, may be the biochemical predecessors of plant waxes.

The number of possible isomeric ketoalkanoic acids varies with the length of the carbon chain and is one less than the corresponding number of possible hydroxy acids because the terminal keto group exhibits aldehydic rather than ketonic reactivity; hence, there are only fourteen possible keto acids corresponding to palmitic acid but fifteen hydroxy isomers.

The ketoalkanoic acids exhibit the characteristics of ketones as well as carboxylic acids. They form derivatives with hydroxylamine, phenylhydrazine, semicarbazide, and similar reagents. They vary in reactivity and physical properties depending on the point of attachment of the ketonic oxygen. Except for two or three of the lowest members of the homologous series the ketoalkanoic acids are white crystalline solids, insoluble in water but soluble in hot organic solvents.

In general, the higher ketoalkanoic acids are stable distillable compounds; however, the 2-keto acids lose carbon dioxide on heating and pass to the next lower saturated acid. When heated with strong aqueous sulfuric acid the 2-keto acids lose carbon dioxide and form aldehydes with one less carbon atom than the original acids. The 3-keto acids likewise lose carbon dioxide on heating, yielding methyl ketones. The 4-keto acids and those with the keto group farther removed from the carboxyl are as stable as the corresponding unsubstituted acids. The 3-keto acids can enolize to some extent but those with keto groups farther removed preserve the ketonic form. Ketoalkanoic acids can be catalytically hy-

TABLE 11
Monoketoalkanoic Acids ^a

Systematic name	M.p., ° C.	Derivative, ° C. or ° C./mm.
2-Ketohexanoic		Acid, b.p. 98/14
4-Ketohexanoic	32	Semicarbazone, m.p. 176
5-Ketohexanoic	13	Acid, b.p. 180/20
5-Ketoheptanoic	46.7	Acid, b.p. 110/16
6-Ketoheptanoic	31-32	
3-Ketooctanoic	73-74	Semicarbazone, m.p. 153
4-Ketooctanoic	53	
5-Ketooctanoic	34	Acid, b.p. 280
6-Ketooctanoic	52	Semicarbazone, m.p. 190
7-Ketooctanoic	29-30	Acid, b.p. 184/15
4-Ketononanoic	69	
7-Ketononanoic	42	
4-Ketodecanoic	70-71	
8-Ketodecanoic	64	
10-Ketohendecanoic	59	Semicarbazone, m.p. 135
2-Ketododecanoic	56.5-57	
3-Ketododecanoic		Ethyl ester, b.p. 164-165/13
9-Ketododecanoic	56	Semicarbazone, m.p. 131
10-Ketododecanoic	72	
2-Ketotridecanoic	62-62.5	
10-Ketotridecanoic	63	
12-Ketotridecanoic	70-71	B.p. 185-186/1
2-Ketotetradecanoic	63.8	
3-Ketotetradecanoic	39-40	Semicarbazone, m.p. 253
4-Ketotetradecanoic	87	Oxime, m.p. 74
10-Ketotetradecanoic	69	
11-Ketotetradecanoic	66-67	Semicarbazone, m.p. 100
13-Ketotetradecanoic		Ethyl ester, m.p. 28-29; b.p. 164-166/1
12-Methyl-10-ketotridecanoic	54-55	
12-Methyl-9-ketotridecanoic	50.5-51	
2-Methyl-12-ketotridecanoic	46.5-47.2	Methyl ester, b.p. 181-183/11
2-Ketopentadecanoic	68-68.5	
4-Ketopentadecanoic	92.6	
11-Ketopentadecanoic	70-71	
14-Ketopentadecanoic	78.4-79.4	Methyl ester, m.p. 43.2-43.8; b.p. 205-206/15
2-Ketohexadecanoic	69	
4-Ketohexadecanoic	91-92	Oxime, m.p. 54
5-Ketohexadecanoic	88	
7-Ketohexadecanoic	78	
8-Ketohexadecanoic	77-78	
9-Ketohexadecanoic	73.5-74.5	

TABLE 11 (*Continued*)

Systematic name	M.p., ° C.	Derivative, ° C. or ° C./mm.
10-Ketohexadecanoic	75-75.8	
11-Ketohexadecanoic	74-75	
14-Methyl-10-ketopentadecanoic	68-69	
9-Ketoheptadecanoic	78.5	Semicarbazone, m.p. 111; amide, m.p. 119
2-Ketooctadecanoic	74.5	Methyl ester, m.p. 54
3-Ketooctadecanoic	99 (dec.)	Semicarbazone, m.p. 295-300; methyl ester, m.p. 49
4-Ketooctadecanoic	97	Semicarbazone, m.p. 126; oxime, m.p. 85; methyl ester, m.p. 48
5-Ketooctadecanoic	87; 91	Methyl ester, m.p. 54.5
6-Ketooctadecanoic	87	Oxime, m.p. 59-61; methyl ester, m.p. 46.5
7-Ketooctadecanoic	83	Methyl ester, m.p. 49
8-Ketooctadecanoic	84	Methyl ester, m.p. 46.5
9-Ketooctadecanoic	83	Semicarbazone, m.p. 118-120; methyl ester, m.p. 47.5
10-Ketooctadecanoic	82.5	Semicarbazone, m.p. 100-101; methyl ester, m.p. 46; ethyl ester, m.p. 41
11-Ketooctadecanoic	82	Methyl ester, m.p. 47
12-Ketooctadecanoic	81.5	Semicarbazone, m.p. 125; methyl ester, 45
13-Ketooctadecanoic	82	Methyl ester, m.p. 47.5
14-Ketooctadecanoic	82	Methyl ester, m.p. 49
15-Ketooctadecanoic	83	Methyl ester, m.p. 53.5
16-Ketooctadecanoic	93	Methyl ester, m.p. 54.5
17-Ketooctadecanoic	87.5	Methyl ester, m.p. 56
16-Methyl-10-ketoheptadecanoic	71.2-72	
10-Ketononadecanoic	86-87	
13-Ketoheneicosanoic	89-90	Semicarbazone, m.p. 104-105
4-Ketodocosanoic	103	
10-Ketodocosanoic	94	
14-Ketodocosanoic	84.5	Oxime, m.p. 49-51
10-Ketotricosanoic	93.5	
10-Ketotetracosanoic	94-94.5	
13-Ketotetracosanoic	95	
13-Ketotriacontanoic	104	
18-Ketononatriacontanoic	110.3-110.6	
13-Ketodotetracontanoic	110	

* Compiled in part by D. Swern (Chapter XIII) and originally published under the title, "Oxygenated Fatty Acids," *Progr. in Chem. Fats Lipids*, 3, 214-241 (1955).

drogenated to yield hydroxy acids or can be converted to saturated acids by the Clemmensen reduction.

Most of our knowledge of the keto fatty acids has been derived from studies of synthetic products which may be prepared by several different methods (see Chapter XIX). The position of the keto group is best determined by converting the acid to the oxime and subjecting the latter to a Beckmann rearrangement followed by hydrolysis and identification of the hydrolytic products.

The melting points of the known monoalkanoic acids from ketohexanoic to ketodotetracontanoic and the melting or boiling points of their principal derivatives are given in Table 11.

Ketopropionic Acid, $\text{CH}_3\text{COCO}_2\text{H}$. Pyruvic or ketopropionic acid is the simplest and one of the most important α -ketoalkanoic acids. It is an intermediate product of the decomposition of sugars in alcoholic fermentation and is further decomposed to acetaldehyde with the elimination of carbon dioxide. In the animal organism it is converted in the liver to the corresponding amino acid, alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$.

Pyruvic acid is a liquid with a penetrating odor; density d_4^{20} 1.267, b.p. 165°C ., f.p. 13°C ., m.p. 13.6°C . It is miscible with water and has a relatively high dissociation constant, 5.6×10^{-3} .

The acid is readily prepared in good yield by distilling tartaric acid in the presence of potassium bisulfate, which was the method whereby it was first produced and is still the best method for its preparation.

Ketobutyric Acid, $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$. β -Ketobutyric or acetoacetic acid, like other β -ketoalkanoic acids is very unstable and because of this instability it is seldom used as such. It is a liquid which boils with decomposition below 100°C .

Acetoacetic acid is normally employed in the form of its salts and esters, especially as the ethyl ester. Ethyl acetoacetate or simply acetoacetic ester, $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$, normally consists of about 8% enol and 92% keto form. It is a colorless, pleasant-smelling liquid, which boils at 181°C . It can be obtained in the form of an unstable crystalline mass by cooling to -78°C . or by careful acidification of its sodium salt and extraction with ethyl ether. However, in this form it decomposes into acetone with the elimination of carbon dioxide.

Acetoacetic ester is among the most useful and widely employed intermediates for the preparation of many organic compounds and has been used technically for the preparation of numerous pyrazolone dyes and of pharmaceuticals such as antipyrine, pyramidone, etc. The use of acetoacetic ester in the synthesis of fatty acids is discussed in Chapter XIX.

Ketopentanoic (Ketovaleric) Acids, $C_5H_8O_3$. All three of the possible isomers of ketovaleric acid have been synthesized. 2-Ketovaleric acid, $CH_3(CH_2)_2COCO_2H$, can be prepared from butyryl chloride by treatment with silver cyanide and hydrolysis of the cyanide. It melts at $179^\circ C$. The 3-keto acid, $CH_3CH_2COCH_2CO_2H$, has been prepared by the action of ethylmagnesium iodide on ethyl cyanoacetate. It is a liquid boiling at $191^\circ C$.

The 4-ketopentanoic or levulinic acid is the simplest γ -ketonic carboxylic acid. It is formed in good yield by heating sugars, particularly hexoses such as fructose (levulose, hence the name levulinic acid), glucose, and galactose with concentrated hydrochloric acid. The reaction is so characteristic for 6-carbon sugars that it can be used for their detection. The reaction is a complicated one and proceeds by way of hydroxymethylfurfural.

Like other γ -ketonic acids levulinic acid can be prepared by reacting α -halogen-substituted fatty acids with acetoacetic ester, followed by alkaline hydrolysis of the condensation product; also by the action of dimethylzinc on the acid chloride of monoethyl ester of succinic acid.

Levulinic acid is a crystalline solid melting at $37.2^\circ C$; density, d_4^{20} 1.1395; refractive index, $n_D^{15.8}$ 1.442; boiling point, $246^\circ C$. It can be distilled without decomposition and it does not lose carbon dioxide as do the β -keto acids, but on continued heating it loses water to form an internal anhydride.

Higher Synthetic Keto Acids. A considerable number of keto saturated fatty acids from ketohexanoic (ketocaproic), $C_6H_{10}O_3$, to ketodotetracontanoic, $C_{42}H_{82}O_3$, have been prepared by various methods. In general only a few of the possible isomers corresponding to each acid have been prepared although eight of the fourteen possible isomers of ketopalmitic acid have been prepared, and Bergström *et al.* (110) have prepared and characterized all sixteen of the possible isomers of ketostearic acid and their methyl esters. Data with respect to the thermal properties of these acids are given in Table 11 and for their crystal properties in Chapter IV. Ralston (131) assembled and described most of the methods of preparation of the higher ketoalkanoic acids in use prior to 1948 and more recently Swern (132) described some additional methods. The more generally applicable of these methods are described in Chapter XIX.

(f) Alkanedioic Acids

The alkanedioic or dicarboxylic acids, although not common constituents of fats and waxes, are nevertheless of considerable importance in the

chemistry of the fatty acids. Oxidative cleavage of the unsaturated fatty acids at the double bond and identification of the fragments have been among the most important methods for establishing the point of unsaturation in the original acid. The reaction is preferably carried out with the ester of the unsaturated acid. If the acid contains only one double bond the cleavage products will consist of a monocarboxylic acid and the half-ester of a dicarboxylic acid. The method was used to establish the position of the double bond in oleic acid. When methyl oleate, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOCH}_3$, is subjected to carefully controlled fission the resulting fragments are nonanoic acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$, and the half-ester of azelaic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOCH}_3$. See Chapters XIII and XIV for detailed discussion of this and similar reactions.

The aforementioned reaction may occur spontaneously through atmospheric oxidation, thus accounting for the presence of dibasic acids which have been detected in linseed oil (133) and in fatty ointments (134) found in ancient Egyptian tombs.

The lower members of the alkanedioic acid series are found in some plants, especially in the foliage and roots, both free and in the form of potassium and calcium salts. Intermediate and higher members of the series have been reported as constituents of certain waxes (Japan wax, sumach berry wax) and natural resins.

The dicarboxylic acids, while not primary constituents of fats, are nevertheless important as metabolic products of these substances. Acids of this type are produced from fats or fatty acids by the process known as ω -oxidation. Some of the lower members of the series which can be synthesized in the animal organism are of importance because of the role they play in the so-called tricarboxylic acid cycle. The reactions involved in this cycle are responsible for the oxidation of carbohydrates and a considerable portion of the fatty acid intermediates.

Owing to the presence of two carboxyl groups in the molecule, the dicarboxylic acids form two series of derivatives (salts, esters, etc.), depending on whether one or both carboxylic groups undergo reaction. Because of their reactivity the alkanedioic acids are employed in the preparation of a variety of fatty derivatives. They react with polyfunctional alcohols and amines to give condensation products and linear polymers. When reacted with a trifunctional alcohol (glycerol) they form thermosetting plastics; with ethylene glycol they may form high molecular weight polyesters; with diamines they form high molecular weight polyamides. The patent literature with reference to methods of producing these polycondensation products is very large, and the claimed uses for

the products (plastics, plasticizers, adhesives, rubber substitutes, cloth coatings, synthetic fibers, etc.,) are numerous. The simple diesters also find many applications, for example, as lubricants, heat-transfer agents, pump fluids, etc.

The older and better known alkanedioic acids are usually referred to by their common names, especially in the trade. Newer acids are usually designated by their systematic names. The latter designation involves the addition of the suffix *dioic* to the straight-chain hydrocarbon from which they may be considered as having been derived; thus oxalic acid, $\text{HOOC}\cdot\text{COOH}$, is called ethanedioic acid, and azelaic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOH}$ is called nonanedioic. In some of the literature they are named on the basis of the longest carbon chain of the acid with numerical prefixes to designate the points of attachment of the carboxyl groups; thus azelaic acid is 1,7-heptanedicarboxylic acid. In the older literature they may be named on the basis of the number of methylene groups in the chain; under this system azelaic acid is designated heptamethylene-1,7-dicarboxylic acid.

The alkanedioic acids form a series corresponding to the general formula, $(\text{CH}_2)_n(\text{COOH})_2$. In the lowest member of the series, oxalic or ethanedioic, the value of n is zero.

The dicarboxylic acids are more soluble in water and have higher melting points than the corresponding monocarboxylic acids. Their solubilities and melting points also exhibit alternation; an acid with an odd number of carbon atoms is more soluble in water than the even-number carbon acid immediately below it. An odd-number carbon acid, on the other hand, has a lower melting point than the even-number carbon acid immediately below it. Some of the lower members exhibit limited solubilities in organic solvents. The corresponding diesters, unlike the acids, do not exhibit alternation in melting points, and between C_7 and C_{32} they lie on a smoothly ascending curve. Various properties of the saturated dicarboxylic acids are collected in Table 12.

Oxalic (Ethanedioic) Acid, $\text{HOOC}\cdot\text{COOH}$. Oxalic acid is the simplest of the alkanedioic acids. It was first prepared by Scheel in 1776 by oxidizing glucose with nitric acid and in 1784 he isolated the acid from rhubarb roots. It occurs in many plants in the form of its potassium, sodium and calcium salts. Algae, molds, lichens, and ferns are rich in oxalic acid but it is also found in many higher plants, for example, as the acid potassium salt in the plants of Oxalidaceae (wood sorrel family) and in the plants of the genus *Rumex* (dock) of the Polygonaceae; as the sodium salt in the plants of the genus *Salicornia* (glasswort) and *Salsola* (saltwort)

TABLE 12 Alkanedioic Acids

Acid	Formula R-(COOH) ₂	For- mula weight ^a	Neutral- ization value ^b	M.p., ° C.	B.p., ° C.	<i>d</i> ₄ ²⁰	<i>n</i> _D ²⁰	Soly. in water at 20° C., g./100 ml.	Ionization constants	
									<i>k</i> ₁ × 10 ⁵	<i>k</i> ₂ × 10 ⁶
Oxalic	(COOH) ₂	90.02	124.5	101, 189 anh.	Sublimes 150	1.653	1.475	10.2	3800	43.7
Malonic	CH ₂ —	104.03	107.8	135.6	dec.	1.6305 ¹⁵		73.5	177	4.5
Succinic	(CH ₂) ₂ —	118.05	95.0	185	235 (dec.)	1.564 ¹³	1.534	6.8	7.36	5.34
Glutaric	(CH ₂) ₃ —	132.06	84.9	97.5	304 (dec.)	1.429 ¹³	1.41878 ^{106.4}	63.9	4.60	5.29
Adipic	(CH ₂) ₄ —	146.08	76.8	153.5	265 ¹⁰⁰	1.366		1.5 ¹⁵	3.90	4.87
Pimelic	(CH ₂) ₅ —	160.10	70.9	105.7	272 ¹⁰⁰	1.329 ¹⁵		5.0	3.33	4.71
Suberic	(CH ₂) ₆ —	174.11	64.4	140	279 ¹¹⁰			0.14 ¹⁶	3.07	4.64
Azelaic	(CH ₂) ₇ —	188.13	59.6	106.5	360 (dec.)	1.029	1.4303 ^{110.6}	0.24	2.82	3.0
Sebacic	(CH ₂) ₈ —	202.14	55.5	134.5	295 ¹⁰⁰		1.422 ^{133.3}	0.17	2.8	3.0
Heptadecanedioic	(CH ₂) ₉ —	216.16	51.9	111						
Dodecanedioic	(CH ₂) ₁₀ —	230.18	48.7	128						
Brassylic	(CH ₂) ₁₁ —	244.19	45.9	113.5						
Tetradecanedioic	(CH ₂) ₁₂ —	258.21	43.4	125.8						
Pentadecanedioic	(CH ₂) ₁₃ —	272.22	41.2	114.7						
Thaspic	(CH ₂) ₁₄ —	286.24	39.2	125.1						
Heptadecanedioic	(CH ₂) ₁₅ —	300.26	37.3	118						
Octadecanedioic	(CH ₂) ₁₆ —	314.27	35.7	124.7						
Nonadecanedioic	(CH ₂) ₁₇ —	328.29	34.1	119.2						
Eicosanedioic	(CH ₂) ₁₈ —	342.30	32.7							
Japanic ^c	(CH ₂) ₁₉ —	356.32	31.4							
Docosanedioic	(CH ₂) ₂₀ —	370.34	30.2	126						
Tricosanedioic	(CH ₂) ₂₁ —	384.35	29.1	127.5						

^a Calculated on basis of International Atomic Weights for 1952.^b The neutralization value of dibasic acids is equal to the number of milligrams of KOH required to neutralize one gram of acid (112.208 × 1000) divided by the molecular weight of the acid.^c This acid probably is tricosanedioic rather than heneicosandioic; see text.

of the Chenopodiaceae; and as the magnesium salt in the leaves of Gramineae. Spinach (*Spinacia oleraceae*) contains 0.31% oxalic, citric, and a small quantity of malic acid in the form of salts (135). The urine of man and animals always contains small quantities of calcium oxalate and larger quantities occur in pathological conditions (oxaluria).

Oxalic acid is poisonous if taken internally; the soluble neutral salts are more toxic than the free acid (136). A poisonous weed, halogeton, which contains oxalic acid, is known to kill livestock grazing on it.

Oxalic acid is produced from many carbohydrate substances when they are fused with alkalis and at one time it was produced commercially by fusing sawdust with caustic soda. The oldest method of preparing the acid is by nitric oxidation of glucose. The process, however, has only become economically feasible during the second quarter of the present century. The largest production of the acid is by the sodium formate process in which carbon monoxide is reacted under pressure with sodium hydroxide and the resulting sodium formate heated to convert it to sodium oxalate with the liberation of hydrogen (137).

Various salts, mono- and diesters, mono- and diamides, and other derivatives are manufactured from oxalic acid and find a variety of uses. The free acid is used as a laundry scour, in dyeing and bleaching reactions in the textile industry, in the leather industry for bleaching and tanning, in the formulation of rust and stain removers, metal polishes, wood cleaners, radiator cleaner compounds, in refining tall oil, and in the manufacture of dyes. The neutral esters are good solvents for nitrocellulose and find limited use in formulating special lacquers for electronic tube manufacture and in certain types of printing inks where they function to prevent the ink from drying on the hot press rolls (137).

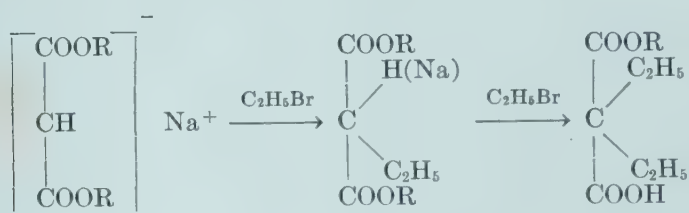
Malonic (Propanedioic) Acid, $\text{CH}_2(\text{COOH})_2$. Malonic acid was first obtained by Dessaignes in 1858 as an oxidation product of malic acid, $\text{HOOCCH}_2\text{CHOHCOOH}$, isolated from the apple (*Pyrus malus*), hence the name. It is a constituent of beet juice and in 1881 was isolated in the form of the calcium salt by E. O. von Lippmann from the scale incrustation formed by the distillation of sugar beet juice.

It is the second member of the series of alkanedioic acids but differs markedly in two respects from its homologs because (a) it easily loses one carboxylic acid group as carbon dioxide, and (b) because of the pronounced reactivity of its methylene group. Both properties arise from the presence of the β -dicarbonyl group, $-\text{COCH}_2\text{CO}-$, which is also present in β -keto acids like acetoacetic acid and in β -diketones.

When heated above 135°C . the acid begins to lose carbon dioxide and

in aqueous solution decarboxylation begins at about 70° C. This instability accounts for the almost negligible use of the acid per se in industrial operations, but it is responsible for its utility in preparing α,β -unsaturated fatty acids.

The pronounced reactivity of the methylene group of malonic acid is also present in most of its functional derivatives, but of these the diethyl ester is used almost exclusively for practical purposes. The esters and nitriles of malonic acid form metallic derivatives (salts) with alkali metals. For preparative purposes these are not isolated from their preparative solutions (anhydrous ethanol). The salts react *in situ* with organic halogen compounds to form the corresponding carbon-substituted malonic ester derivatives. The reaction can be illustrated as follows:



If dihalogen compounds are used, cyclic dicarboxylic esters are produced. When reacted with acid chlorides, keto-acid esters are produced. Condensation of malonic acid derivatives with carbonyl compounds (aldehydes and ketones) leads to the formation of α,β -unsaturated fatty acids.

Malonic acid derivatives are used in the manufacture of barbiturates, vitamin B₁ (thiamin), vitamin B₆ (pyridoxine), various amino acids (ornithine, tryptophane, glutamic acid, etc.), and various hypnotics. The monoammonium, bismuth, and copper salts have therapeutic properties.

Succinic (Butanedioic) Acid, (CH₂)₂(COOH)₂. Various authors attribute the discovery of succinic acid to Agricola who obtained it in 1550 by distilling amber, the fossil resin of *Pinus succinifera*. Agricola referred to amber by its Latin name, *succinum* (Agricola: *De Natura Fossilium*, rev. 1558), rather than by its Arabic name, *ambar*, hence the name succinic acid. Others attribute the discovery of succinic acid to Lémery, who obtained it by the same method and from the same source in 1675. Succinic acid is obtained in 3 to 8% yield, together with other acids (acetic, butyric, valeric and caproic) when amber is distilled to produce colophony. Part of the acid is believed to be present in amber in the form of an ester condensation product and part as a vinyl-type polymerization product.

Succinic acid is present in many plants (unripe gooseberries, grapes, beet juice, rhubarb), in certain types of lignite, fossil woods and resins, turpentine oils, etc. It is formed by the bacterial fermentation of calcium malate and ammonium tartrate which were once important methods of manufacturing succinic acid; in the fermentation of proteins (casein); during alcoholic fermentation (probably from glutamic acid); and in the chemical (nitric acid) and biochemical oxidation of fats, spermaceti, and other waxes.

Succinic acid is manufactured principally by hydrogenation of maleic anhydride or fumaric acid by several different methods all of which give good yields of the free acid or the anhydride.

The colorless crystalline acid melts at 185°C ., sublimes under a pressure of 1 to 3 mm. Hg at $132\text{--}152^{\circ}\text{C}$., and undergoes dehydration at 235°C . It is soluble in water, ethanol, diethyl ether, anhydrous glycerol, acetone, and various aqueous mixtures of glycerol and acetone.

Succinic acid is a very reactive substance displaying most of the characteristic reactions of dicarboxylic acids and additional special reactivity by virtue of the presence of two adjacent methylene groups attached to two unsaturated carbonyls, $\text{—}(\text{O:})\text{C—CH}_2\text{—CH}_2\text{—C}(\text{:O})\text{—}$. The acid can be halogenated to form *meso*-dibromosuccinic acid or an acid chloride (succinoyl chloride); condensed with ketones and aldehydes (Stobbe condensation); dehydrated to form a cyclic anhydride; esterified with mono- and polyhydric alcohols; reacted with aromatic compounds in the presence of aluminum chloride (Friedel-Craft reactions); reacted with ammonia and mono- and polyamines to yield succinimides, and with sulfur compounds (allyl isothiocyanate).

Because of its marked reactivity succinic acid is used as an intermediate in the manufacture of medicinals, perfumes, dyes, photographic chemicals, insect repellents, lubricant additives, alkyd resins, plastics, plasticizers, resin stabilizers, adhesives, etc. (138).

Glutaric (Pentanedioic) Acid, $(\text{CH}_2)_3(\text{COOH})_2$. Glutaric acid has been found in beet juice and the water in which raw sheep's wool has been washed, from which latter source it was obtained by Buisine and Buisine (139) in 1888. It received its name because of its relationship to glutamic acid, $\text{HOOC}(\text{CH}_2)_2\text{CHNH}_2\text{COOH}$, and tartaric acid, $(\text{CHOH})_2\text{—}(\text{COOH})_2$.

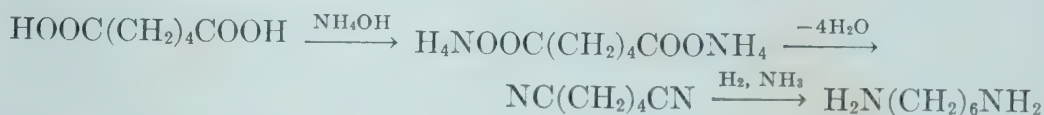
Glutaric acid is similar to its lower homologs but less available and hence of lesser importance. It is prepared by nitric acid oxidation of various cyclic compounds, chiefly cyclopentanol and cyclopentanone or by catalytic air oxidation of the same compounds. It may be prepared in the laboratory from trimethylene bromide via the cyanide.

The acid is encountered as a fission product of the oxidation of unsaturated fatty acids having a double bond in the appropriate position.

Adipic (Hexanedioic) Acid, $(\text{CH}_2)_4(\text{COOH})_2$. Adipic acid, despite its name (Latin *adipis*, fat), is not a constituent of normal fats but has been found in these substances as a product of oxidative rancidity. The acid was obtained in 1884 by Dieterle and Hell (140) when castor oil was oxidized with nitric acid. It has been found in beet juice and as an oxidation product of Russian mineral oil which is rich in cyclohexane.

Adipic acid was first synthesized in 1902 from tetramethylene bromide and a year later Zélinisky (141) reported its syntheses by the oxidation of cyclohexanol and cyclohexanone with nitric acid. Since that time many methods have been investigated for the production of the acid by oxidation of cyclohexane and cyclohexene and their derivatives (cyclohexanol, cyclohexanone, cyclohexenyl acetate) with nitric acid or potassium permanganate. Commercially it is produced by catalytic oxidation (oxides of vanadium, manganese, molybdenum) of cyclohexanone or cyclohexanol with nitric acid or nitrous oxides. It is available in 99.6% (min.) purity, packed in 50-lb. multiply bags. The commercial product melts at 152.1°C .

Adipic acid has a number of minor uses as a substitute for tartaric acid in baking powders and as plasticizers and gelatinizing agents in the form of its esters, but its most important use is in the manufacture of nylon. For use in the last-mentioned process it is converted into hexamethylenediamine via adiponitrile as indicated by the following reactions:



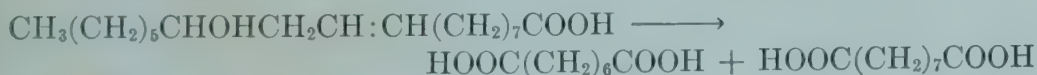
Hexamethylenediamine is then reacted in stoichiometric proportions with adipic acid in water or methanol to give hexamethylenediammonium adipate, called "6-6 salt." The latter product is heated under very precise conditions to induce the desired degree of polymerization. The solid polymer is subsequently remelted and extruded through a spinneret (melt spinning) to form fibers (Type 6 nylon).

Hexamethylenediamine can be produced by other reactions, namely, from furfural by conversion to furan, reduction of furan to tetrahydrofuran, conversion of the latter to 1,4-chlorobutane, reaction of the latter with sodium cyanide to yield adiponitrile, etc. It can also be produced via adiponitrile from butadiene derived from natural gas or petroleum.

Pimelic (Heptanedioic) Acid, $(\text{CH}_2)_5(\text{COOH})_2$. Pimelic acid, from the Greek *pimelē* (fat), is not a normal constituent of fats but it has been isolated from such substances as a product of oxidation. It was obtained in 1884 by Ganttner and Hell (142) as a product of oxidation of ricinoleic acid. It has also been found in the urine of herbivorous animals.

Pimelic acid was first obtained by oxidation of suberone (cycloheptanone). It can be prepared by a number of reactions including a novel one which involves opening the ring of salicylic acid by 1,4-addition of hydrogen with sodium in amyl alcohol. It can also be prepared from cyclohexanone by chlorination, conversion of the chlorinated product to the cyanide, followed by hydrolysis with sodium hydroxide.

Suberic (Octanedioic) Acid, $(\text{CH}_2)_6(\text{COOH})_2$. Suberic acid derives its name from the Latin *suber* or cork from which it was first produced by nitric acid oxidation. In 1841 Tilley (143) obtained the acid by nitric acid oxidation of castor oil. The acid can be prepared by prolonged oxidation of castor oil and ricinoleic acid or its esters with relatively dilute nitric acid at high temperature (144). Azelaic acid is produced at the same time as indicated by the following equation:



The two acids are separated by vacuum distillation of the methyl esters.

Suberic acid can also be prepared by oxidation of cyclooctene (C_8H_{14}) which is obtained by partial hydrogenation of cyclooctatetraene (C_8H_8). The latter is made commercially by means of controlled polymerization of acetylene. The acid has also been produced by various other methods including the electrolysis of potassium ethyl glutarate, reaction of trimethylene bromide with magnesium and carbon dioxide, etc.

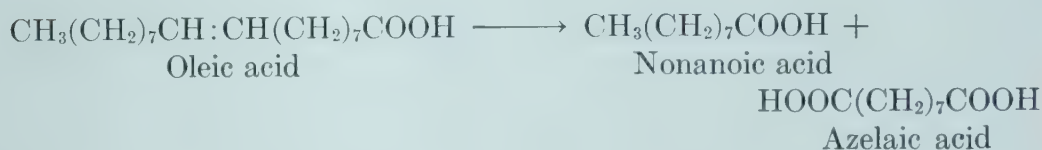
The acid is used to a limited extent in the manufacture of alkyd resins. Condensation polymerization of suberic acid with diamines yields polyamides. The product (octamethylenediammonium suberate or "8-8 salt") formed by reacting octamethylenediamine with suberic acid after polymerization yields a nylon (Type 8) which finds application in coatings, textile finishes, and adhesives where toughness, flexibility, and hydrocarbon resistance are required. Type 8 nylon can be thermoset to form alcohol-insoluble, relatively infusible compositions which retain the flexibility and other desirable properties of the original polymer.

Azelaic (Nonanedioic) Acid, $(\text{CH}_2)_7(\text{COOH})_2$. Azelaic acid is perhaps the best known, but not necessarily the most important of the high-molecular-weight alkanedioic acids. Two explanations have been ad-

vanced for the origin of the name of this acid, namely, that it is obtained (a) by the action of nitric acid, hence *az* from *azote* (nitrogen), on olive oil (Greek, *elaion*) (145), and (b) by nitric (*azotic*) acid oxidation of elaidic acid (146).

The acid is not a component of normal fats but it has been detected among the products of oxidative rancidity of these substances (133,134, 147). It has also been reported to result from the hydrolysis of an unidentified substance in mold spores (148), and from the oxidation of keratin (149).

The acid was prepared by Ganttner and Hell (150) in 1881 and by Saytzeff (151) in 1885 by oxidation of oleic acid with potassium permanganate. Oxidative fission of oleic acid can be carried out to give relatively good yields of azelaic acid but the reaction cannot be controlled to produce stoichiometric quantities of the primary fission products indicated by the following equation:



Both of the primary fission products undergo further oxidation to produce shorter chain acids prior to the complete oxidation of the oleic acid.

Other monoethenoic acids, as well as di- and other polyethenoic acids yield azelaic acid when oxidized with potassium permanganate (see Chapter XIII).

Azelaic acid can also be prepared by ozonization of oleic acid and decomposition of the ozonide, and by dichromate-sulfuric acid oxidation of dihydroxystearic acid. It has been synthesized by the malonic synthesis from pentamethylene dibromide and diethyl sodiomalonate. The acid can be prepared in 30 to 35% yields from commercial grades of castor oil by nitric acid oxidation of ricinoleic acid.

Kabayashi and Miyazaki (151a) described a method for preparing azelaic acid from commercial grade oleic acid involving the conversion of the acid to the chlorohydroxyoleate by the action of chlorine in sodium hydroxide solution, then to dihydroxystearic acid by treatment with aqueous sodium hydroxide, and chromic acid oxidation of the dihydroxy acid to yield azelaic acid. The authors obtained a yield of 37% dihydroxystearic acid from oleic and a yield of 45% of azelaic acid from dihydroxystearic acid or an over-all yield of less than 17%. The acid is

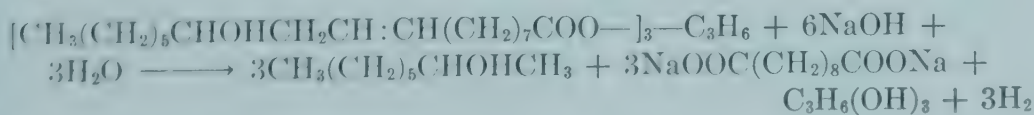
produced commercially by oxidative cleavage of oleic acid with chromic acid or by ozonolysis.

A considerable tonnage of azelaic acid is manufactured for conversion into simple esters, branched-chain esters, and polyhydric alcohol esters. The simple esters (dioctyl, etc.) find applications as plasticizers, especially for vinyl chloride resins; the branched-chain esters (isoamyl, 2-ethylhexyl, iso-octyl) are employed as lubricants (jet engines) and for other military applications. The diesters serve as bases for special greases, particularly when jelled with a lithium soap (lithium stearate or 12-hydroxystearate); and as diffusion pump oils (dioctyl, iso-octyl, etc.). Linear polymers of azelaic acid and glycol are useful plasticizers for vinyl chloride resins, rubber, nitrocellulose, and other resins. Azelaic acid, and more particularly sebacic acid, is used as a partial or complete replacement of phthalic anhydride in the formulation of oil-modified glycerol or pentaerythritol alkyd resins (152).

Sebacic (Decanedioic) Acid, $(\text{CH}_2)_8(\text{COOH})_2$. The name, sebacic, appears to be derived from the Latin *sebaceus* (tallow candle) or *sebum* (tallow) in reference to the tallowy feel of sebacic acid and its use in the manufacture of candles. From the industrial point of view sebacic acid manufacture of candles. From the industrial point of view sebacic acid According to Kadesch (152) this acid is produced in excess of 20 million pounds annually by alkali fission of castor oil.

Sebacic acid was prepared by Bouis (153) in 1855 by the dry distillation of castor oil in the presence of caustic soda. The method was investigated by Boedtke (154) who suggested a possible mechanism for the reaction; and shortly thereafter by Verkade *et al.* (155). With increasing industrial demand for sebacic acid improved methods of its production from castor oil became the subject of various patents (156–159). The various methods specify that the reaction should be carried out with caustic soda in (a) solid form, (b) aqueous solution, and (c) suspended in a high-boiling liquid such as white mineral oil.

In the fusion process castor oil and caustic soda are heated to 250–300° C. Sebacic acid and capryl alcohol (2-octanol) are formed according to the following equation:



At some stage of the reaction the double bond migrates from the 9-position.

In another process (157) castor oil is slowly added to a solution of caustic soda maintained at 245°C . in a reaction vessel connected to a distillation column. The capryl alcohol which is formed simultaneously with sebacic acid passes off with some water vapor into a condensing system. The hydrogen evolved in the reaction is vented and a separator returns the water to the reaction mixture to maintain its constant boiling point. After the reaction is complete, the residue containing the sodium sebacate is drawn off and dispersed in water. Acidification of the aqueous layer yields sebacic acid as a fine white precipitate in approximately 40% yield by weight of castor oil charged to the reaction kettle.

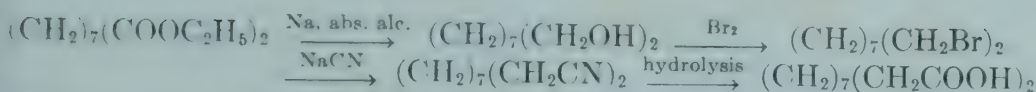
Another patent (159) claims that 84% yields are obtained when the reaction is carried out with aqueous sodium hydroxide at 275°C . in the presence of cadmium oxide.

Sebacic acid can be prepared by other methods including the oxidation of 10-hendecenoic acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_8\text{COOH}$, and the electrolysis of an aqueous solution of potassium ethyl adipate, $\text{KOOC}(\text{CH}_2)_4\text{COOC}_2\text{H}_5$, to yield diethyl sebacate, $\text{C}_2\text{H}_5\text{OOC}(\text{CH}_2)_8\text{COOC}_2\text{H}_5$.

Sebacic acid and its derivatives have a variety of industrial uses as plasticizers, lubricants, diffusion pump oils, and in the manufacture of alkyd resins, polyamide esters, cosmetics, fruit essences, candles, etc., which, in general, are the same or similar to those mentioned under azelaic acid. The acid is used in place of adipic acid in the reaction with hexamethylenediamine to produce a polyamide, the so-called "6-10 nylon," having especially high water resistance. The polyhydric alcohol esters of sebacic acid are particularly valuable in alkyd resin applications where flexibility is required, for example, in coated fabrics.

A commercial product called isosebacic acid has recently been placed on the market. It is produced synthetically from butadiene, $\text{CH}_2:\text{CHCH}:\text{CH}_2$, and consists of a mixture of normal and branched-chain sebacic acids conforming approximately to the composition 6-10% normal sebacic acid, 12-18% 2,5-diethyladipic acid, and 72-80% 2-ethylsuberic acid, $\text{HOOC}(\text{CH}_2)_5\text{CHC}_2\text{H}_5\text{COOH}$. The product is claimed to have application for the production of vinyl resin plasticizers, polyamide molding and extrusion plastics and adhesives, alkyd resins, ester lubricants for jet-propelled aircraft, polyesters used in the manufacture of glass-reinforced plastics, polyurethane resins for foamed plastics, and synthetic rubber.

Hendecanedioic Acid, $(\text{CH}_2)_9(\text{COOH})_2$. Hendecanedioic acid has been prepared by chromic oxidation of 11-hydroxyhendecanoic acid in acetic acid solution. It has also been prepared from azelaic acid via the nitrile method involving the following reactions:

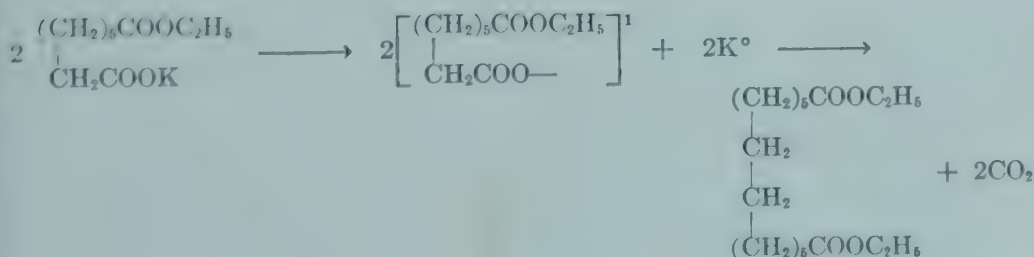


Chuit (160) and Chuit and Hausser (161) using either azelaic or sebacic acid and applying the nitrile or malonic acid method synthesized all of the alkanedioic acids from C_{11} to C_{19} . Application of the malonic acid method affords a particularly convenient method of synthesizing the higher dibasic acids.

Dodecanedioic Acid, $(\text{CH}_2)_{10}(\text{COOH})_2$. Dodecanedioic acid has been prepared from 11-hydroxyhendecanoic acid by conversion of the hydroxy acid to the corresponding bromo acid and the bromo acid to the nitrile followed by hydrolysis of the last-mentioned product to the desired dibasic acid. It has also been prepared from sebacic acid via the nitrile as described above for the preparation of hendecanedioic acid from azelaic acid.

Brassylic (Tridecanedioic) Acid, $(\text{CH}_2)_{11}(\text{COOH})_2$. Brassylic acid was prepared by Fileti and Ponzio (162) in 1893 by nitric acid oxidation of erucic and brassidic acids, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOH}$. Oxidation of behenolic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOH}$ with the same reagent also yields brassylic acid. The acid has been synthesized by condensation of ethyl 11-bromohendecanoate and diethyl sodiomalonate, followed by saponification and partial decarboxylation of the resulting tricarboxylic acid. Chuit (160) synthesized the acid from sebacic acid via the nitrile as outlined under hendecanedioic acid.

Tetradecanedioic Acid, $(\text{CH}_2)_{12}(\text{COOH})_2$. Tetradecanedioic acid has been synthesized by Chuit (160) as previously mentioned, also by Carmichael (163) who obtained it by electrolysis of potassium ethyl suberate. This method (Kolbe's electrolytic method) is applicable to the synthesis of all of the even carbon atom dibasic acids above malonic acid. The method involves the electrolysis between platinum electrodes of a concentrated solution of the potassium salt of the half-ester of the dibasic acid in accordance with the following equation for the synthesis of tetradecanedioic acid.



The method is completely analogous to the electrolytic synthetic of hydrocarbons from the monocarboxylic acids.

Thapsic (Hexadecanedioic) Acid, $(\text{CH}_2)_{14}(\text{COOH})_2$. Thapsic acid was isolated by Canzoneri (164) in 1883 from the resinlike extract of the dried roots of the Mediterranean "deadly carrot," *Thapsia garganica* (family Umbelliferae). It was synthesized by Carmichael (163) in 1922 by electrolysis of potassium ethyl azelate, $\text{KOO}(\text{CH}_2)_7\text{COOC}_2\text{H}_5$, and a few years later by Chuit (160) by the malonic acid method.

Octadecanedioic Acid, $(\text{CH}_2)_{16}(\text{COOH})_2$. Octadecanedioic acid has been prepared by electrolysis of potassium ethyl sebacate, $\text{KOO}(\text{CH}_2)_8\text{COOC}_2\text{H}_5$, and by the malonic acid method.

Japan Wax Acids. Japan wax or tallow is obtained from one of several species of sumach tree (*Rhus* sp.) cultivated in Japan, Formosa, China, Indo-China and India for the wax which is contained in the mesocarp of the berries. In Japan the principal species grown for this purpose is *R. succedanea*. Japan wax, strictly speaking, is not a wax but a fat or vegetable tallow consisting largely of tripalmitin. According to Tsujimoto (165) the component fatty acids consist of 77% palmitic, 5% stearic and arachidic, 12% oleic and a trace of linoleic acid, and 5 to 7% of dibasic acids.

The exact identity of the dibasic acids in Japan wax has been the subject of much research and little agreement since they were first detected by Eberhardt (166) in 1888. The acid isolated by Eberhardt was believed to be heneicosanedioic, $(\text{CH}_2)_{19}(\text{COOH})_2$. Geitel and van der Want (167) concluded that the acid more nearly corresponded to docosanedioic, $(\text{CH}_2)_{20}(\text{COOH})_2$. Schaal (168) several years later reported that Japanese acid consisted principally of heneicosanedioic acid, $(\text{CH}_2)_{19}(\text{COOH})_2$, together with some eicosanedioic and nonadecanedioic, $(\text{CH}_2)_{17}(\text{COOH})_2$.

Ruzicka *et al.* (169) obtained cycloeicosanone in substantial quantities on distilling the thallium salts of the dibasic acids of Japan wax; this appeared to substantiate Schaal's observation that the principal acid was heneicosanedioic.

Flaschenträger and Halle (170), however, isolated a dibasic acid melting at 127.5°C ., which corresponded to tricosanedioic, $(\text{CH}_2)_{21}(\text{COOH})_2$, and were unable to obtain any evidence of the presence of heneicosanedioic acid.

In 1931, Tsujimoto (171) reported the isolation of two dibasic acids from Japan wax, one of which melted at 123.5°C . and corresponded to the formula for tricosanedioic, and another corresponding to that for docosanedioic acid. In a subsequent publication Tsujimoto reaffirmed

TABLE 13
Alkanedioic Acids: Synthetic and from Japan Wax

Acid, R-dioic	Formula, R—(COOH) ₂	M.p., ° C.	Method	Author
<i>Synthetic</i>				
Nonadecane-	(CH ₂) ₁₇ —	119.2	Malonic acid	Chuit ^a
Eicosane-	(CH ₂) ₁₈ —	123		Chuit <i>et al.</i> ^a
Heneicosane-	(CH ₂) ₁₉ —	112	Electrolysis	Ruzicka <i>et al.</i> ^b
Docosane-	(CH ₂) ₂₀ —	123.8	Electrolysis	Fairweather ^c
		127	Nitrile	Shiina ^d
Tricosane-	(CH ₂) ₂₁ —			
Tetracosane-	(CH ₂) ₂₂ —	127	Nitrile	Shiina ^d
Pentacosane-	(CH ₂) ₂₃ —			
Hexacosane-	(CH ₂) ₂₄ —	123.5	Electrolysis	Fairweather ^c
Triacontane-	(CH ₂) ₂₈ —	123.3	Electrolysis	Fairweather ^c
Tetratriacontane-	(CH ₂) ₃₂ —	123	Electrolysis	Fairweather ^c
<i>Japan Wax</i>				
Nonadecane-		117.5		Schaal ^e
Eicosane-		not given		Schaal ^e
Heneicosane-		not given		Schaal, ^e Eberhardt ^f
Docosane-		117.8		Geitel <i>et al.</i> ^g
		114		Tsujimoto ^h
		126		Shiina ^d
Tricosane-		122–123.5		Tsujimoto ^h
		127.5		Flaschenträger <i>et al.</i> ⁱ
		125.5–126.3		Schuette <i>et al.</i> ^j

^a P. Chuit, *Helv. Chim. Acta*, **9**, 264–278 (1926); P. Chuit and J. Hausser, *ibid.*, **12**, 850–859 (1929).

^b L. Ruzicka, M. Stoll, and H. Schinz, *Helv. Chim. Acta*, **11**, 670–686 (1928).

^c D. A. Fairweather, *Proc. Roy. Soc. Edinburgh*, **45**, 283–285 (1925); **46**, 71–75 (1926); *Phil. Mag.*, [7], **1**, 944–950 (1926).

^d S. Shiina, *J. Soc. Chem. Ind. Japan, Suppl. bind.*, **43**, 173–174 (1940); **42**, 147 (1939).

^e R. Schaal, *Ber.*, **40**, 4784–4788 (1907).

^f L. A. Eberhardt, *Inaug. Diss.*, Strassbourg, 1888.

^g A. C. Geitel and G. van der Want, *J. prakt. Chem.*, [2], **61**, 151–156 (1900).

^h M. Tsujimoto, *Bull. Chem. Soc. Japan*, **6**, 325–337 (1931); **10**, 212–219 (1935).

ⁱ B. Flaschenträger and F. Halle, *Z. physiol. Chem.*, **190**, 120–140 (1930).

^j H. A. Schuette and R. M. Christenson, *Oil & Soap*, **19**, 209–211 (1942).

his conclusions regarding the identity of the dibasic acids of Japan wax. In 1940, Shiina (172) reported the isolation of a dibasic acid from Japan wax which melted at 125.7–126.3° C. and corresponded to the formula for docosanoic acid. Still later, Schuette and Christenson (173) reported the results of a reinvestigation of Japan wax in the course of which they isolated a dibasic acid melting at 125.5–126.3° C. which they concluded corresponded to the formula for tricosanedioic acid, (CH₂)₂₁(COOH)₂.

Several of the aforementioned dibasic acids from Japan wax, have also been synthesized (169,172,174), and in at least one case by two different methods. The various alkanedioic acids allegedly isolated from Japan wax and the corresponding synthetic acids are compared in Table 13.

Despite the present availability of relatively pure parent materials, highly specific methods of synthesis, and refined techniques for identification, the exact identity and composition of the mixture of dibasic acids designated as Japanic acid are as yet not known with certainty.

4. Alkenoic (Olefinic) Acids

In addition to the saturated or alkanolic acids discussed in the previous section there exists in nature, especially in fats and waxes, a considerable number of unsaturated acids which are differentiated from the former by the presence of one or more double or triple bonds in their carbon skeletons. The presence of unsaturated bonds in these acids markedly alters their chemical and physical properties compared with those of their unsaturated counterparts. The presence of unsaturated carbon-carbon linkages imparts special biological activity to some of these acids and to others it imparts properties which are of utilitarian value from the industrial point of view.

The unsaturated acids found in nature are very heterogeneous with respect to the type and degree of their unsaturation. The presence of one or more of these acids in the form of glycerides imparts to many fats characteristic properties and special utility.

Certain of the unsaturated acids are widely distributed in vegetable, animal, and marine fats and waxes, while others are restricted to a few species or even to one species. As more and more species of plant fats have been investigated the degree of heterogeneity of the naturally occurring unsaturated acids has been found to be much greater than was assumed a few years ago and it is now suspected that it is even more diverse than our present knowledge indicates.

Of the two classes of naturally occurring unsaturated acids, ethylenic and acetylenic, those containing only double bonds are of far more frequent occurrence than those containing only triple bonds, while those containing both types of unsaturated are encountered even less frequently.

Because of the large number and diversity of the unsaturated fatty acids it is necessary to group them into classes for ease of description and comparison of their chemical and physical properties. The alkenoic (ethylenic, olefinic) acids have been classified on the basis of the number

of carbon-to-carbon double bonds in the normal carbon chain, and are designated as monoalkenoic (monoethenoic); alkadienoic(dienoic, diethenoic); alkatrienoic (trienoic, triethenoic); etc. The nomenclature is derived from that of the alkene hydrocarbons under Rule 8 of the Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry (3) and is followed in the present work.

(a) *Monoalkenoic Acids, $C_nH_{2n-2}O_2$*

The monoalkenoic acids, also termed monoethenoic, monoethylenic, and monoolefinic acids, contain two less hydrogen atoms than the corresponding saturated or alkanolic acids and can, therefore, be represented by the formula indicated above. This group encompasses the largest number of known naturally occurring and synthetic unsaturated acids. The large number of theoretically possible monoethenoic acids results not only from differences in the length of the carbon chain, but also from the occurrence of positional isomerism of the carbon-to-carbon double bond and from the fact that for each position isomer (except the terminal one) there exists two geometric (*cis* and *trans*) isomers. A relatively short-chain acid such as hexenoic has no less than seven isomers, namely, four positional isomers of which three exist in two geometric forms. With increasing chain length the number of theoretical possible isomers, increases correspondingly; thus octadecenoic acid has thirty-one isomers, namely, sixteen positional isomers of which fifteen may be represented by two geometrical forms. In general, only a few, and sometimes only one, of the theoretically possible isomers of a given monoethenoic acid have been found in nature, but all of the others may be known in the form of synthetic products.

The majority of the unsaturated acids that have been isolated from plant and animal sources have a double bond between the ninth and tenth carbon atoms. Of these, oleic, $C_{18}H_{34}O_2$, and palmitoleic, $C_{16}H_{30}O_2$, are by far the most commonly occurring and best known of the monoethenoic acids. Both are widely distributed in nature and, in frequency of occurrence, constitute the predominant acids of the monoalkenoic series as stearic and palmitic acids constitute the predominant acids of the saturated alkanolic series. A few of the naturally occurring monoethenoic acids have their double bonds at some position other than between the ninth and tenth carbon atoms. In general, these acids constitute minor components of the fats in which they are found and are limited to a few species of plants and animals. An exception to this statement is the occurrence of petroselinic, $C_{18}H_{34}O_2$, and erucic, $C_{22}H_{42}O_2$, acids in certain

seed fats. These acids, which have their double bonds between the 6,7- and 13,14-carbon atoms, respectively, have been found to comprise 70 to 80% of the total fatty acids of a few seed fats. Other exceptions will be noted later under specific acids.

In addition to the straight-chain or normal monoalkenoic acids there are known among the naturally occurring monounsaturated acids a few examples of branched-chain acids (angelic and tiglic), and substituted acids (ricinoleic or hydroxyoleic).

Relatively few monoalkenoic acids of low molecular weight are found in nature. Crotonic acid, $\text{CH}_3\text{CH}:\text{CHCOOH}$, occurs in the seed oil of *Croton tiglium*; angelic acid, $\text{CH}_3\text{CH}:\text{C}(\text{CH}_3)\text{COOH}$, has been found in the oil of angelica root, *Angelica archangelica*, and its *trans*-isomer, tiglic acid, has been found in the oil of Roman camomile, *Anthemis nobilis*, and in *Croton tiglium*. A hexenoic acid has been reported to occur in peppermint oil.

Some of the chemical and physical properties of the better known monoalkenoic acids are given in Table 14.

Propenoic (Acrylic) Acid, $\text{C}_3\text{H}_4\text{O}_2$. Acrylic or 2-propenoic acid, $\text{CH}_2:\text{CHCOOH}$, is the lowest member of the straight-chain monoalkenoic series of acids. It is not a constituent of natural fats and waxes, but it and its branched-chain isomer, methacrylic acid, $\text{CH}_2:\text{C}(\text{CH}_3)\text{COOH}$, are industrially important. The acid was first obtained by the oxidation of acrolein, $\text{CH}_2:\text{CHCHO}$, in -843, and its tendency to polymerize was noted as early as 1872, but it was not until the 1930's that it achieved significant industrial importance.

Acrylic acid is a pungent, corrosive liquid, miscible with water and ethanol. It is a stronger acid than acetic. It readily undergoes polymerization, sometimes producing a violent reaction when not controlled.

The acid can be readily prepared by oxidation of acrolein with silver oxide and it has been prepared by the catalytic oxidation (vanadic acid) of this aldehyde with air at 20–34° C. Other methods of preparation include (a) conversion of ethylene chlorohydrin to cyanohydrin followed by alkaline hydrolysis, dehydration, and acidification; (b) dehydrohalogenation of β -chloropropionic acid; (c) dealcoholation of β -ethoxypropionic acid; (d) hydrolysis of acrylonitrile; (e) from allyl alcohol by bromination, oxidation to the dibromo acid, and debromination with zinc.

Technically the acid is prepared by (a) oxidation of acrolein under various conditions; (b) oxidation of methyl vinyl ketone with hypohalites; (c) hydrolysis of acrylonitrile; (d) hydrolysis of ethylene cyanohydrin; (e) dehydrohalogenation of β -chloropropionic acid; and (f) catalytic hydrolysis of maleic anhydride.

There is little technical use of acrylic acid per se because of its tendency to undergo spontaneous polymerization. The acid is usually converted to its final polymerized or other reacted form as soon as possible after preparation. In the form of its polymeric acids, esters, salts, etc., it has a wide variety of industrial uses (175).

Butenoic Acids, $C_4H_6O_2$. Two straight-chain position isomers of butenoic acid are theoretically possible and both are well known. They are 2-butenic (crotonic) acid and 3-butenic (vinylacetic) acid. The former, but not the latter, is capable of existing in two geometrically isomeric forms, both of which are known, namely, crotonic and isocrotonic acid.

A third position isomer is theoretically possible but it contains a branched chain. This acid, 2-methylpropenoic or methacrylic acid, has the same empirical formula ($C_4H_6O_2$) as the other butenoic acids. It is treated in Section 4,g together with other branched-chain alkenoic acids.

Crotonic (2-butenic) acid, $CH_3CH:CHCOOH$, exists in two geometric forms which are designated respectively, crotonic or *trans*-2-butenic acid, melting at $71.5^\circ C.$, and isocrotonic or *cis*-2-butenic acid, melting at $15.5^\circ C.$ This type of isomerism which is typical of the entire series of monoalkenoic acids is discussed in Chapter III.

Both geometric isomers have been reported to be constituents of the seed oil of *Croton tiglium*, a small, tropical, evergreen tree indigenous to the East Indies. According to Flaschenträger and Wolffersdorff (176) the acids of croton oil are: oleic, 56%; linoleic, 29%; palmitic, 1.3%; and stearic, 0.5%. Small quantities of volatile acids (formic, acetic) and traces of butyric, valeric, and tiglic acids, possibly derived from nonglyceride constituents of the oil, have also been reported to be present.

Crotonic acid was prepared as early as 1863, but it was not until 1936 that it became available in the United States in commercial quantities (177). The acid is not responsible for the purgative and other physiological reactions of croton oil. These are attributed to the presence in the oil of an alcohol-soluble resinous material dissolved in the glycerides. Crotonic acid is readily metabolized and it can be synthesized by the animal organism from β -hydroxybutyric acid, $CH_3CHOHCH_2COOH$; also the reverse transformation has been noted in the fasting rat (178). The acid has been found in an infertile soil in Texas and as a product of bacterial metabolism of β -hydroxybutyric acid.

Crotonic acid is a crystalline solid soluble in ethanol, toluene, and acetone. It forms a eutectic mixture (m.p. $-3^\circ C.$) with isocrotonic acid containing 30% crotonic acid.

The acid can be prepared by several methods which are also applicable

TABLE 14
Alkenoic Acids, $C_nH_{2n-2}O_2$

Systematic name	Common or other name	Formula	Formula weight ^a	Neutralization value ^a		M.p., ° C.	B.p., ° C.	d_4^{20}	n_D^{20}
				value ^a	Iodine value ^a				
2-Propenoic	Acrylic	$C_3H_4O_2$	72.06	778.55	352.25	12.3	141.9	1.0621 ¹⁶	1.4224
2-Butenoic (<i>trans</i> ?)	Crotonic	$C_4H_6O_2$	86.09	651.71	294.86	72	189	1.018	1.4228 ^{16,17}
2-Butenoic (<i>cis</i> ?)	Isocrotonic	$C_4H_6O_2$	86.09	651.71	294.86	14	171.9 (dec.)	1.0312 ¹⁸	1.4457
3-Butenoic	Vinylacetic	$C_4H_6O_2$	86.09	651.71	294.86	-39	163	1.0131 ¹⁵	1.4257 ¹⁸
2-Pentenoic	β -Ethylacrylic	$C_5H_8O_2$	100.11	560.40	253.55	8	200 ¹⁷	0.9921 ¹⁶	1.4501 ⁵
3-Pentenoic	β -Pentenoic	$C_5H_8O_2$	100.11	560.40	253.55		193		
4-Pentenoic	Allylacetic	$C_5H_8O_2$	100.11	560.40	253.55	< -18	189	0.9843 ¹⁶	1.4341 ^{7,16}
2-Hexenoic	Isohydrosorbic or β -propylacrylic	$C_6H_{10}O_2$	114.14	491.54	222.39	32	217	0.965	1.4467 ¹⁶
3-Hexenoic	Hydrosorbic	$C_6H_{10}O_2$	114.14	491.54	222.39	12	208	0.9610 ²²	1.4255
4-Hexenoic	γ -Hexenoic	$C_6H_{10}O_2$	114.14	491.54	222.39	0	206.5	0.9658	1.4367
5-Hexenoic	δ -Hexenoic	$C_6H_{10}O_2$	114.14	491.54	222.39		203	0.9610	1.4343
2-Heptenoic	α -Heptenoic	$C_7H_{12}O_2$	128.17	437.74	198.06		121 ^{11,15}	0.9576	1.4488
3-Heptenoic	β -Heptenoic	$C_7H_{12}O_2$	128.17	437.74	198.06		226		
5-Heptenoic	δ -Heptenoic	$C_7H_{12}O_2$	128.17	437.74	198.06		223		
6-Heptenoic	ϵ -Heptenoic	$C_7H_{12}O_2$	128.17	437.74	198.06	-6.5	225	0.9521 ¹⁷	1.4425 ¹¹
2-Octenoic (<i>cis</i>)	<i>cis</i> - α -Octenoic	$C_8H_{14}O_2$	142.19	394.57	178.52		154 ²²	0.9807	1.4587
2-Octenoic (<i>trans</i>)	<i>trans</i> - α -Octenoic	$C_8H_{14}O_2$	142.19	394.57	178.52		143 ¹⁶	0.9451 ⁵	1.462
3-Octenoic	β -Octenoic	$C_8H_{14}O_2$	142.19	394.57	178.52		140 ¹⁹	0.942	1.4456 ²²
2-Nonenoic (<i>cis</i>)	<i>cis</i> - α -Nonenoic	$C_9H_{16}O_2$	156.22	359.14	162.49		144 ¹⁸	0.9316 ¹⁵	1.4594
2-Nonenoic (<i>trans</i>)	<i>trans</i> - α -Nonenoic	$C_9H_{16}O_2$	156.22	359.14	162.49		154.5 ¹⁵	0.9361 ¹⁵	1.4635 ¹⁵
3-Nonenoic	β -Nonenoic	$C_9H_{16}O_2$	156.22	359.14	162.49		114 ²	0.9290	1.4484
2-Decenoic	Obtusilic	$C_{10}H_{18}O_2$	170.24	329.55	149.10		148 ^{4,6}	0.9280	1.4616
4-Decenoic	Caproleic	$C_{10}H_{18}O_2$	170.24	329.55	149.10		143 ¹⁶	0.9197	1.4497
9-Decenoic	9-Undecenoic, 9-undecylenic	$C_{11}H_{20}O_2$	184.27	304.47	137.75	11.4	129 ¹	0.9238 ¹⁵	1.4488
9-Hendecenoic									
10-Hendecenoic	10-Undecenoic, 10-undecylenic	$C_{11}H_{20}O_2$	184.27	304.47	137.75	24.5	275	0.9076 ²⁵	1.4464 ²⁰
2-Dodecenoic	2-Lauroleic	$C_{12}H_{22}O_2$	198.30	282.93	128.01		164 ²	0.9130	1.4639
3-Dodecenoic	Linderic	$C_{12}H_{22}O_2$	198.30	282.93	128.01	1.0	170 ¹³	0.9081	1.4529
5-Dodecenoic	5-Lauroleic	$C_{12}H_{22}O_2$	198.30	282.93	128.01			0.9130 ¹⁶	1.4535 ¹⁵
11-Dodecenoic	11-Lauroleic	$C_{12}H_{22}O_2$	198.30	282.93	128.01		143 ²	0.9030 ²⁶	1.4510

2-Undecenoic	$C_{11}H_{20}O_2$	212.32	264.24	119.55	169 ¹	0.8995 ¹⁰	1.4612
12-Tetradecenoic	$C_{13}H_{24}O_2$	212.32	264.24	119.55	192 ¹⁵		
12-Tetradecenoic	$C_{13}H_{24}O_2$	212.32	264.24	119.55	38	0.9024	1.4557
4-Tetradecenoic	$C_{14}H_{26}O_2$	226.35	247.45	111.93	185 ¹³	0.9046	1.4552
5-Myristoleic	$C_{14}H_{26}O_2$	226.35	247.45	111.93		0.9018	1.4519
9-Tetradecenoic	$C_{14}H_{26}O_2$	226.35	247.45	111.93			
2-Pentadecenoic	$C_{15}H_{28}O_2$	240.37	233.40	105.60	198 ⁸		
14-Pentadecenoic	$C_{15}H_{28}O_2$	240.37	233.40	105.60			
2-Hexadecenoic	$C_{16}H_{30}O_2$	254.40	220.53	99.78	45		
7-Hexadecenoic	$C_{16}H_{30}O_2$	254.40	220.53	99.78	$\begin{cases} 21 \\ 33 \end{cases}$		
9-Hexadecenoic	$C_{16}H_{30}O_2$	254.40	220.53	99.78	0.5		
9-Hexadecenoic	$C_{16}H_{30}O_2$	254.40	220.53	99.78	31		
2-Heptadecenoic	$C_{17}H_{32}O_2$	268.43	209.01	94.57	57.5		
cis-6-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	30	0.8681 ⁴⁰	1.4533 ⁴⁰
trans-6-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	54		
cis-9-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	13.4 (α)	0.8905	1.45823
trans-9-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	16.3 (β)		
Elaidic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	46.5	0.8568 ⁷⁰	1.4405 ⁷⁰
cis-11-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	14.5		
trans-11-Octadecenoic	$C_{18}H_{34}O_2$	282.45	198.63	89.87	44	0.8563 ⁷⁰	1.4406 ⁷⁰
cis-9-Eicosenoic	$C_{19}H_{36}O_2$	310.50	180.69	81.75	22		
cis-11-Eicosenoic	$C_{19}H_{36}O_2$	310.50	180.69	81.75	52-53		
trans-11-Eicosenoic	$C_{19}H_{36}O_2$	310.50	180.69	81.75			
cis-11-Docosenoic	$C_{21}H_{40}O_2$	338.56	165.72	74.98			
cis-13-Docosenoic	$C_{21}H_{40}O_2$	338.56	165.72	74.98	34.7	0.85321 ⁷⁰	1.4438 ⁷⁰
trans-13-Docosenoic	$C_{21}H_{40}O_2$	338.56	165.72	74.98	61.9	0.85002 ⁷⁰	1.44349 ⁷⁰
cis-15-Tetracosenoic	$C_{23}H_{46}O_2$	366.61	153.04	69.24	42.5-43		
trans-15-Tetracosenoic	$C_{23}H_{46}O_2$	366.61	153.04	69.24	65.5		
cis-17-Hexacosenoic	$C_{25}H_{50}O_2$	396.66	142.16	64.32	45		
cis-21-Triacontenoic	$C_{29}H_{58}O_2$	450.76	124.46	56.31			

* Calculated on the basis of International Atomic Weights for 1952.

to the preparation of other α,β -unsaturated acids. These include (a) oxidation of the corresponding unsaturated aldehyde with reagents which do not attack double bonds, e.g., oxidation of crotonic aldehyde, $\text{CH}_3\text{CH}:\text{CHCHO}$, with silver oxide or catalytically with air or oxygen; (b) dehydrohalogenation of α -bromo acid esters (e.g., $\text{CH}_3\text{CH}_2\text{CHBrCOOR}$) with alcoholic potash or a tertiary amine; (c) hydrolysis of the corresponding unsaturated cyanide prepared from the bromide with cuprous cyanide, e.g.,



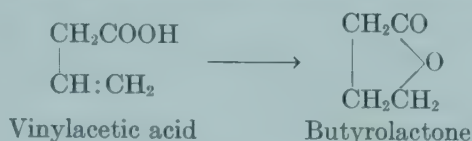
(d) from malonic ester and aldehyde, e.g., paraldehyde in acetic anhydride or acetaldehyde and secondary amines, also by condensing acetaldehyde in dry ethyl ether solution with malonic acid in the presence of pyridine. Crotonic acid can also be prepared in the laboratory by isomerizing vinylacetic acid, $\text{CH}_2:\text{CHCH}_2\text{COOH}$, by warming it with 50% sulfuric acid. The acid is produced commercially by catalytic oxidation of crotonaldehyde with air or oxygen.

The esters, amide, anilide, anhydride, halides, etc., of crotonic acid are well known and at times some of them have been used extensively in industry, e.g., during World War II up to 100 tons a month of *n*-butyl crotonate was used in Germany in the production of dibutyl β,β -thiodibutyrate, $\text{S}:[\text{CH}(\text{CH}_3)\text{CH}_2\text{COOC}_4\text{H}_9]_2$ as a softening agent in synthetic rubber. Today the world production of crotonic acid appears to be relatively small and its industrial use negligible (177).

Vinylacetic (3-butenic) acid, $\text{CH}_2:\text{CHCH}_2\text{COOH}$, is the second of the two possible position isomers of butenoic acid, but unlike 2-butenic acid it exists only in one geometric form. It does not occur in nature. It is a colorless liquid, slightly soluble in water, and completely miscible with ethanol and diethyl ether. It can be prepared in the laboratory by (a) treating allyl magnesium bromide with carbon dioxide, and (b) by hydrolysis of allyl cyanide after first protecting the double bond by bromination, followed by dehalogenation of the dibromo acid with zinc.

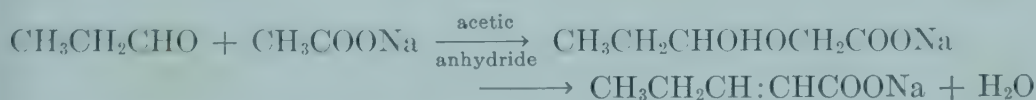
Unlike acrylic and crotonic acids, vinylacetic acid exhibits the reactions of a carbonyl and an olefin independently of one another because of the lack of conjugation in the unsaturated linkages. It adds bromine more rapidly and halogen acids less rapidly than crotonic acid, which is characteristic of other β,γ -unsaturated acids as compared to α,β -unsaturated acids.

Boiling with dilute acids or alkalis converts vinylacetic acid to crotonic acid, whereas reaction with concentrated alkalis yields two molecules of acetate by shifting the double bond and splitting the α,β -unsaturated compound as it is formed. Vinylacetic acid readily changes into butyrolactone which is the inner ester of γ -hydroxybutyric acid.



Pentenoic Acids, $\text{C}_5\text{H}_8\text{O}_2$. All three of the position isomers of pentenoic acid are known. They are termed 2-pentenoic acid or β -ethylacrylic acid, $\text{CH}_3\text{CH}_2\text{CH}:\text{CHCOOH}$; 3-pentenoic, also called β -pentenoic acid, $\text{CH}_3\text{CH}:\text{CHCH}_2\text{COOH}$; and 4-pentenoic or allylacetic acid, $\text{CH}_2:\text{CHCH}_2\text{CH}_2\text{COOH}$, respectively. The first two acids also exist in two geometric forms. None of these acids is found as a constituent of natural fats or waxes.

β -Ethylacrylic (*cis*-2-pentenoic) acid is a liquid at ambient temperatures. It is soluble in water to the extent of 15.89 g./100 ml. and is readily soluble in ethanol and diethyl ether. The acid can be prepared like other α,β -unsaturated acids by (a) dehydrohalogenation of the corresponding α -halogenated acid, in this case by starting with commercially available *n*-amyl alcohol, oxidation to valeric acid, halogenation followed by dehydrohalogenation; (b) condensation of an aldehyde with sodium acetate in the presence of acetic anhydride, in this case starting with propanal as per the following equation:



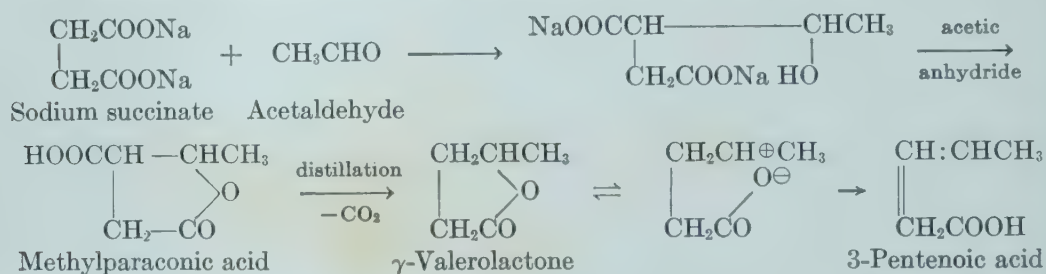
(c) condensation of an aldehyde with malonic ester in the presence of a secondary amine, in this case propanal in the presence of pyridine containing 0.5% piperidine.

The *trans*-isomer can be prepared by treating the *cis*-isomer with iodine. The *trans*-isomer is a liquid boiling at 106°C . at 15 mm. pressure and a reported density of 1.454¹⁵.

β -Pentenoic or *cis*-3-pentenoic acid is a colorless liquid which is moderately soluble in water and readily soluble in ethanol and diethyl ether. It cannot be prepared by the ordinary methods of dehydrohalogenation because the corresponding β -halogen acid loses hydrogen halide (HX) with the α -hydrogen. On the other hand, a γ -halogenated acid when treated

with alkali forms a γ -lactone instead of the desired β,γ -unsaturated acid. The acid can be prepared by reducing the lactone of levulinic (γ -keto-valeric) acid, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$. The reactions of levulinic acid indicate that it exists largely in the form of its lactone.

In common with other β,γ -unsaturated acids, 3-pentenoic acid can be prepared by distilling the proper alkylparaconic acid obtained by a modification of the Perkin reaction from an aldehyde, sodium succinate, and acetic anhydride. In this case methylparaconic acid is distilled to yield the required acid. The reactions involved in preparing β,γ -unsaturated acids by this method may be illustrated by the following equations using acetaldehyde to obtain the required methylparaconic acid.

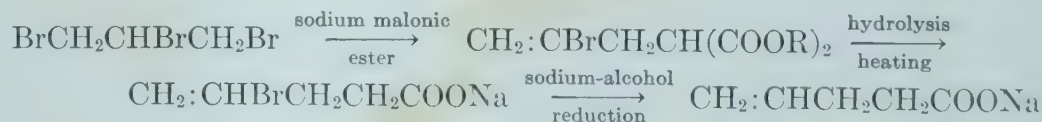


In addition to the γ -lactone of the same carbon chain length as the β,γ -unsaturated acid, anhydrides of two unsaturated dibasic acids are formed, apparently through opening of the lactone ring of the methylparaconic acid followed by rearrangement of the molecule.

By substituting propanal, butanal, etc., for acetaldehyde there is obtained ethylparaconic acid, propylparaconic acid, etc., which on distillation yield 3-hexenoic acid, 3-heptenoic acid, etc.

Methylparaconic acid can also be prepared by reducing the ethyl ester of acetosuccinic acid according to the method of Fichter and Pfister (179).

Allylacetic or 4-pentenoic acid is a colorless liquid which is slightly soluble in water and readily soluble in ethanol and diethyl ether. It exists in only one geometric form. The acid is easily prepared by the malonic ester or acetoacetic ester synthesis for acids using allyl bromide, $\text{CH}_2:\text{CHCH}_2\text{Br}$; also by the malonic ester synthesis using tribromopropane according to the following reactions:



The reactions of allylacetic acid are similar to those of the lower homologs which have no conjugated system of double bonds. With sulfuric acid it yields methyl butyrolactone (γ -valerolactone).

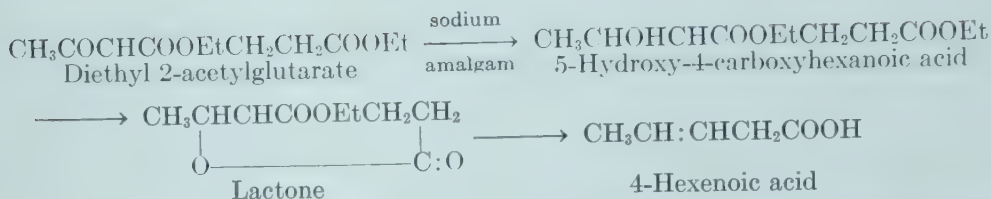
Hexenoic Acids, $C_6H_{10}O_2$. Four position isomers of hexenoic acid are possible, namely, 2-hexenoic or isohydrosorbic acid, $CH_3(CH_2)_2CH:CHCOOH$; 3-hexenoic or hydrosorbic acid, $CH_3CH_2CH:CHCH_2COOH$; 4-hexenoic acid, $CH_3CH:CH(CH_2)_2COOH$; and 5-hexenoic acid, $CH_2:CH(CH_2)_3COOH$. All four of the acids are known and one of them, 2-hexenoic, has been reported to occur in Japanese peppermint oil. All but one, 5-hexenoic acid, are capable of existing in two geometric forms.

2-Hexenoic or isohydrosorbic acid is a white crystalline solid melting at $32^\circ C$. It is slightly soluble in water, soluble in ethanol, and very soluble in diethyl ether.

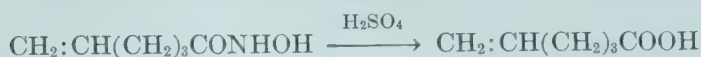
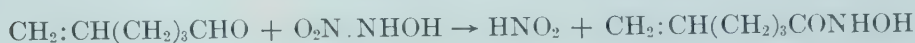
The acid can be prepared from *n*-caproic acid, $CH_3(CH_2)_4COOH$, via the α -bromo acid, and by heating 3-hexenoic acid with a solution of alkali which results in migration of the double bond toward the carboxyl group. Both of these methods result in mixtures of 2-hexenoic and 3-hexenoic acids with the former predominating. It can also be prepared by heating the condensation product of butanal with malonic acid. Condensation of butanal with malonic acid in the presence of pyridine containing 0.5% piperidine gives predominantly the 2-isomer with some 3- and 4-isomers.

3-Hexenoic or hydrosorbic acid is obtained by the distillation of ethyl paraconic acid in the same manner that 3-pentenoic acid is obtained from methyl paraconic acid. Formation of the acid is accompanied by 3-caprolactone. The acid can also be obtained by the partial reduction of sorbic or 2,4-hexadienoic acid, $CH_3CH:CHCH:CHCOOH$, which reaction also yields some 2- and 4-hexenoic acid. The relative proportions of the three acids depend on the conditions of reduction. Dehydrohalogenation produces a mixture of 2- and 3-hexenoic acids as mentioned above. The acid gives the usual reactions of β,γ -unsaturated acids including rearrangement and splitting by alkalies and formation of a lactone when treated with sulfuric acid.

4-Hexenoic acid is produced in substantial amounts along with 3-hexenoic acid on partial reduction of sorbic acid. It is also obtained by decarboxylation of the product of reaction between 1-bromo-2-butene and ethyl sodiomalonate. Distillation of 2-hydroxy-2-methyladipic acid yields a mixture of 4- and 5-hexenoic acids. Perhaps the best method of preparing the acid is from the diethyl ester of 2-acetylglutarate which can be reduced with sodium amalgam to 5-hydroxy-4-carboxyhexanoic acid, the latter converted to the lactone, which is then decarboxylated by distillation to yield the desired acid in accordance with the following reaction:



5-Hexenoic acid is formed by treating 6-aminocaproic acid with nitrous acid. A small amount of the 4-isomer is produced at the same time. The acid can also be prepared from cyclohexanone by rupturing the ring by the action of light or other reagent on an alcoholic solution of the lactone which yields 5-hexenal and caproic acid. The unsaturated aldehyde is treated with nitrohydroxylamine to convert it to the corresponding hydroxamic acid which is then treated with sulfuric acid to give 5-hexenoic acid (180).



It can also be prepared from 1-bromo-3-butene by reaction with ethyl sodiomalonate.

Heptenoic Acids, C₇H₁₄O₂. Four of the five possible position isomers of heptenoic acid have been prepared. None of them has been found as a constituent of natural fats or waxes. In general, the methods that have been used to prepare the heptenoic acids are similar to those applied for the preparation of the corresponding hexenoic acids.

2-Heptenoic acid has been prepared, along with the 3-isomer, by dehydrohalogenation of 2-bromoheptanoic acid with quinoline. The two acids are separated by first treating the mixture to convert the 3-isomer to the lactone. It can also be prepared by oxidizing 2-heptenal, CH₃(CH₂)₃CH:CHCHO, with silver oxide in alkaline solution.

3-Heptenoic acid can be prepared by distillation of propyl paraconic acid in the same manner as the previously described 3-hexenoic and 3-pentenoic acids are obtained from ethyl paraconic and methyl paraconic acid, respectively. It has also been prepared by the malonic acid synthesis starting with *n*-valeraldehyde.

5-Heptenoic acid has been synthesized by converting 5-heptenal, CH₃CH:CH(CH₂)₃CHO, to the hydroxamic acid and treatment of the copper salt of this acid with sulfuric acid (180). It has also been prepared by reaction of 4-chlorobutyric acid, ClCH₂(CH₂)₂COOH, with the

sodium derivative of acetoacetic ester, $\text{CH}_3\text{C}(\text{ONa})\text{:CHCOOC}_2\text{H}_5$, to give acetyladipeic acid which is reduced to 2-(1-hydroxyethyl) adipic acid. The last-mentioned acid on distillation yields 5-heptenoic acid. The reaction is analogous to that involved in the preparation of the previously described 4-hexenoic acid.

6-Heptenoic acid has been prepared by the malonic ester synthesis and also by the action of nitrous acid on 7-aminoheptanoic acid. It has also been observed as one of the products of electrolysis of the half-ester of suberic acid (174).

Octenoic Acids, $\text{C}_8\text{H}_{14}\text{O}_2$. Six position isomers of octenoic acid are possible, but only two are known, both from synthesis as none has been found as a constituent of natural fats or waxes.

2-Octenoic acid, $\text{CH}_3(\text{CH}_2)_4\text{CH:CHCOOH}$, has been prepared by condensation of hexanal, $\text{CH}_3(\text{CH}_2)_4\text{CHO}$, with malonic acid in the presence of pyridine (181). *cis*-2-Octenoic acid can be converted to the corresponding *trans*-acid by the action of iodine.

3-Octenoic acid, $\text{CH}_3(\text{CH}_2)_3\text{CH:CHCH}_2\text{COOH}$, was prepared by Delaby and Lecomte (182) by reaction of hexanal and malonic acid.

The ethyl ester of 7-octenoic acid, $\text{CH}_2\text{:CH}(\text{CH}_2)_5\text{COOC}_2\text{H}_5$, is reported to be one of the products produced by electrolysis of potassium ethyl azelate, $\text{KOOC}(\text{CH}_2)_7\text{COOC}_2\text{H}_5$ (163).

Nonenoic Acids, $\text{C}_9\text{H}_{16}\text{O}_2$. Only two of the seven possible position isomers of nonenoic acid are known, both as the result of synthesis.

2-Nonenoic acid, $\text{CH}_3(\text{CH}_2)_5\text{CH:CHCOOH}$, was first prepared by Fittig and Schneegans (183) in 1885 by the Perkin reaction between heptanal, acetic anhydride, and sodium acetate. Its synthesis from heptanal, $\text{CH}_3(\text{CH}_2)_5\text{CHO}$, and malonic acid in the presence of piperidine and in the presence of pyridine has been described (184). It has also been prepared by the oxidation of 2-nonenal, $\text{CH}_3(\text{CH}_2)_5\text{CH:CHCHO}$, with silver oxide in alkaline solution. The *trans*-isomer has been prepared by treatment of the *cis*-form with iodine.

3-Nonenoic acid, $\text{CH}_3(\text{CH}_2)_4\text{CH:CHCH}_2\text{COOH}$, was prepared by Delaby and Lecomte (182) by the condensation of heptanal and malonic acid in the presence of piperidine.

Decenoic Acids, $\text{C}_{10}\text{H}_{18}\text{O}_2$. Eight positionally isomeric decenoic acids are possible of existence and of these four are known, two from natural sources and two through synthesis. With the exception of crotonic (2-butenoic) acid, the decenoic acids appear to be the lowest molecular weight monoalkenoic acids which have been found in natural fats although lower acids have been reported to be present in essential oils, e.g.,

2-hexenoic acid in Japanese peppermint oil. 9-Decenoic (caproleic) acid has been found in the milk fats of all animals in which efforts have been made to detect it. It is reported to represent 0.2% or less of the total fatty acids in such fats. A second C_{10} -unsaturated acid, namely, 4-decenoic or obtusilic acid, has been reported from one source, a Korean plant.

2-Decenoic acid, $CH_3(CH_2)_6CH:CHCOOH$, has been prepared synthetically by condensing octanal with malonic acid in the presence of pyridine.

3-Decenoic acid, $CH_3(CH_2)_5CH:CHCH_2COOH$, was prepared by Fittig and Schneegans (183) in 1885 by distillation of hexyl paraconic acid. The only data recorded for it is its melting point, $10^\circ C$.

4-Decenoic (obtusilic) acid, $CH_3(CH_2)_4CH:CH(CH_2)_2COOH$, was isolated in 1937 by Toyama (185) and by Komori and Ueno (186). It was obtained from the seed oil of the Korean spice bush (*Lindera obtusiloba*) from which the name of the acid is derived. The acid was isolated in very small quantity (2.9 g. from 5 kg. of oil). The length of the carbon chain was determined by Komori and Ueno by reduction to capric acid, $CH_3(CH_2)_8COOH$, and the position of the double bond by oxidation with potassium permanganate which gave caproic acid, $CH_3(CH_2)_4COOH$, and succinic acid, $HOOC(CH_2)_2COOH$, as fission products.

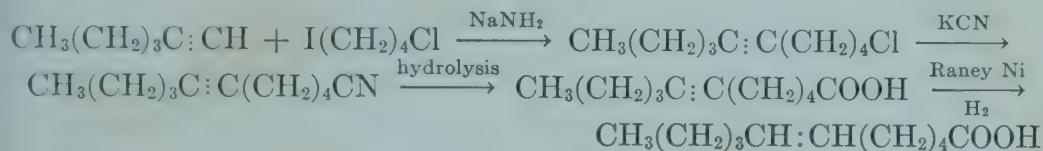
9-Decenoic (caproleic) acid, $CH_2:CH(CH_2)_7COOH$, was first suspected by Smedley (187) in 1912 to be a constituent of butterfat but it was not until ten years later that it was isolated by Grün and Wirth (188) and its structure determined by ozonization of its methyl ester. An additional eleven years elapsed before Bosworth and Brown (189) verified the structure of the acid and provided quantitative data with respect to the extent of its presence in butterfat. Since then various other workers (190) have shown that 9-decenoic acid occurs to the extent of 0.1–0.3% in butterfat. The same acid has been detected in human milk fat (ca. 0.1%) by Bosworth and Brown (191), in goat milk fat by Riemenschneider and Ellis (192), in mare milk fat by Hilditch and Jasperson (193), and in Indian buffalo milk fat by Achaya and Hilditch (194).

Toyama and Tsuchiya (195) isolated from sperm head oil an unsaturated acid which yielded azelaic acid, $HOOC(CH_2)_7COOH$, and formic acid, $HCOOH$, on oxidative fission with potassium permanganate on the basis of which they assumed the acid to be 9-decenoic.

Hendecenoic (Undecenoic, Undecylenic) Acids, $C_{11}H_{20}O_2$. Hendecenoic acids are not found in natural fats and oils but one of them, 10-hendecenoic acid, is produced by pyrolysis of ricinoleic acid and

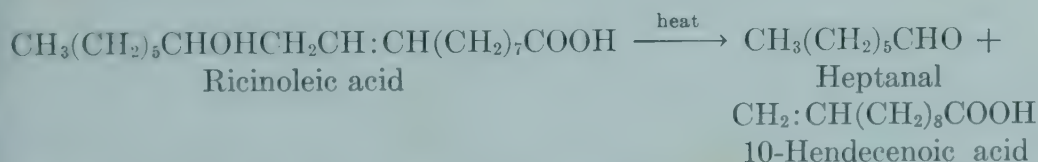
castor oil and finds considerable use in the pharmaceutical and perfume industries.

6-Hendecenoic (*cis*-6-undecenoic) acid, $\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$, was synthesized by Ahmed, Bumpus, and Strong (195a) in 1948 from *n*-butylacetylene, $\text{CH}_3(\text{CH}_2)_3\text{C}:\text{CH}$, and 1-chloro-4-iodo-*n*-butane, as indicated in the following equations:



9-Hendecenoic (9-undecylenic) acid, $\text{CH}_3\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, has been prepared by the debromination of 9-bromo-9-hendecenoic acid, $\text{CH}_3\text{CH}:\text{CBr}(\text{CH}_2)_7\text{COOH}$, with sodium in ethanol and with zinc and propionic acid. The bromo acid was prepared by the action of hydrogen bromide on hendecynoic acid, $\text{CH}_3\text{C}:\text{C}(\text{CH}_2)_7\text{COOH}$.

10-Hendecenoic (10-undecylenic) acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_7\text{COOH}$, has been prepared by the malonic acid synthesis (196), the pyrolysis of ricinoleic acid, and vacuum distillation of castor oil, but it is produced commercially chiefly by the pyrolysis of castor oil under selective conditions. During the pyrolysis of ricinoleic acid or castor oil, cleavage occurs between the eleventh and twelfth carbon atoms accompanied by migration of the hydrogen of the hydroxyl group and a shift of the double bond to yield heptanal and 10-hendecenoic acid.



The pyrolysis of castor oil was investigated as early as 1827 by Bussy and Lecanu (197); heptanal was identified as one of the products of pyrolysis by Bussy (198) as early as 1845, and a hendecenoic acid by Krafft (199) in 1877. The identity of the acid as 10-hendecenoic (10-undecylenic) was established by Becker (200) in 1878 and was confirmed by Perkin (201) and by Brunner (202) in 1886. The pyrolysis reaction has been investigated by many others (203) since then, chiefly with a view to improving the yields and purity of the fission products.

10-Hendecenoic, which is known in the trade as 10-undecylenic acid or simply undecylenic acid, is a colorless crystalline mass or a colorless to yellowish liquid, insoluble in water, slightly soluble in chloroform, and

miscible in all proportions with ethanol and diethyl ether. The acid has been used for many years as an intermediate in the manufacture of perfume ingredients, especially the alcohol obtained by hydrogenation of ethyl and butyl undecylenate and various derived ketones.

The acid and its salts have unusually good fungistatic action, particularly the sodium (204) and zinc salts. The latter salt has been widely used in the treatment of athlete's foot. Claims have also been made that the mercury, aluminum, and bismuth salts also have valuable pharmaceutical applications (205).

10-Hendecenoic acid is a useful starting material for the preparation of other acids and related compounds. Hydrogenation reduces it to decanoic acid, $\text{CH}_3(\text{CH}_2)_9\text{COOH}$. Its dibromide on treatment with alcoholic potassium hydroxide yields 10-hendecynoic acid, $\text{HC}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$, which in turn on fusion with potassium hydroxide at 180°C . rearranges to 9-hendecynoic acid, $\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_7\text{COOH}$. Addition of hydrobromic acid in diethyl ether solution follows Markonikoff's rule, that is, the primary product is 9-bromohendecanoic (9-bromoundecanoic) acid, whereas in toluene addition leads primarily to the production of 10-bromohendecanoic acid. On oxidative fission undecylenic acid yields sebacic acid, $\text{HOOC}(\text{CH}_2)_8\text{COOH}$.

Dodecenoic Acids, $\text{C}_{12}\text{H}_{22}\text{O}_2$. At least half of the ten possible position isomers of dodecenoic acid are known, three from natural sources and several others as the result of synthesis.

2-Dodecenoic acid, $\text{CH}_3(\text{CH}_2)_8\text{CH}:\text{CHCOOH}$, has been prepared by the reaction of decanal with malonic acid in the presence of pyridine.

4-Dodecenoic (linderic) acid, $\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_2\text{COOH}$, has been isolated from the seed oils of several Asiatic plants. It was first obtained by Iwamoto (206) in 1921 from tohaku oil, the seed oil of the Korean spice bush (*Lindera obtusiloba*) from which it also derives its name. The same acid was isolated by Tsujimoto (207) from the seed oil of *Lindera hypoglauca*, and subsequently by Toyama (185) and by Komori and Ueno (186) from the seed oil of *Lindera obtusiloba*, who also established its constitution and determined its physical properties. Still later, Hata (208) obtained the same acid from several Formosan seed oils. The plants in which linderic acid has been found are members of the Lauraceae in which lauric acid is the main component of the seed fats.

5-Dodecenoic acid, $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$, was suspected by Lexow (209) in 1918 to be a constituent of herring oil, but it was not until ten years later that the acid was found by Hilditch and Lovern (210) to constitute 4% of the fatty acids of the head oil of the sperm

whale (*Physeter macrocephalus*). In 1935 Toyama and Tsuchiya (211) reported the isolation of a dodecenoic acid from sperm whale head oil and found it to occur in traces in sperm whale blubber oil. These authors reported the acid to be 5-dodecenoic. The acid has been called lauroleic acid which is most unfortunate as this name, if used at all, should be reserved for 9-dodecenoic acid because of its constitutional relation to lauric and oleic acids.

9-Dodecenoic acid, $\text{CH}_3(\text{CH}_2)\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, or a related dodecenoic acid was found by Raimann (212) to be a constituent of cochineal wax (*Coccus cacti*) as early as 1885; in 1935 such an acid was isolated by Kono and Maruyama (213) from Japanese coccid wax. These authors suggested that the acid was 9-dodecenoic, but there appears some doubt with respect to its exact identity.

In 1924, Grün (214) suggested the presence of a dodecenoic acid in milk fat but Bosworth and Brown (189) were unable to verify its presence in this medium and Reimenschneider and Ellis (192) were unable to detect it in goat milk fat. Hilditch *et al.* (215) however, established its presence in various cow milk fats to the extent of 0.1–0.5 mole per cent, and also its identity as 9-dodecenoic acid. Baldwin and Longenecker (216) found it to the extent of 0.2 mole per cent in cow colostrum fat and Hansen and Shorland (217) demonstrated a seasonal variation of 0.2–0.4 mole per cent of this acid in New Zealand butters. It has also been found to comprise 0.2 mole per cent of the milk fat of the Indian buffalo (194).

11-Dodecenoic acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_9\text{COOH}$, has been prepared by converting 1-bromo-10-decene, $\text{CH}_2:\text{CH}(\text{CH}_2)_7\text{CH}_2\text{Br}$, to 11-dodecenenitrile and hydrolyzing it to yield the desired acid.

Tridecenoic Acids, $\text{C}_{13}\text{H}_{24}\text{H}_2$. No tridecenoic acid has been noted as a constituent of natural fats and waxes and of the eleven possible position isomers only two appear to have been synthesized, namely, the α - and ω -unsaturated acids.

2-Tridecenoic acid, $\text{CH}_3(\text{CH}_2)_9\text{CH}:\text{CHCOOH}$, has been prepared by the reaction of undecanal with malonic acid in the presence of pyridine.

12-Tridecenoic acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_{10}\text{COOH}$, has been prepared by the reaction of 1-bromo-10-undecene and diethyl malonate in the presence of sodium.

Tetradecenoic Acids, $\text{C}_{14}\text{H}_{26}\text{O}_2$. At least three tetradecenoic acids have been identified from natural sources. These acids although present in very small amounts, generally less than 1%, appear to be widely distributed in nature and have been found in animal depot and milk fats, marine animal oils, and some plants of Asiatic origin.

4-Tetradecenoic (tsuzuic) acid, $\text{CH}_3(\text{CH}_2)_8\text{CH}:\text{CH}(\text{CH}_2)_2\text{COOH}$, was isolated by Tsujimoto (207) from the seed fats of *tsuzu* (*Litsea* or *Tetradenia glauca*) and benzoin shrub (*Lindera hypoglauca*) and was later identified by the same author (218) as 4-tetradecenoic acid and named tsuzuic acid. The same acid was isolated by Toyama (185) and by Komori and Ueno (186) from the seed oil of the spice bush, *Lindera obtusiloba*.

5-Tetradecenoic (physeteric) acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$, was isolated in 1923 by Tsujimoto (219), who reported its presence in sperm whale and dolphin oils. On complete reduction the acid gave myristic acid, and on oxidative fission it yielded *n*-nonanoic (pelargonic) acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$, and glutaric acid, $\text{HOOC}(\text{CH}_2)_3\text{COOH}$, thus establishing its identity as 5-tetradecenoic acid. Two years later the same authors verified the identification. The acid was subsequently isolated from sperm whale head and blubber oils (220,221), sardine oil, pilot whale oil, and sperm blubber oil (214,222), and from human hair fat (16). The acid is reported to represent 14% by weight of the total fatty acids of sperm whale head oil and 4% of the blubber oil (221).

9-Tetradecenoic (myristoleic) acid, $\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, was reported in 1925 by Armstrong and Hilditch (223) to be present in whale oil to the extent of about 1.4% together with an isomeric acid with a double bond nearer the carboxyl group. The latter acid was subsequently identified as 5-tetradecenoic. In 1928, Hilditch and Lovern (210) confirmed the identity of 9-tetradecenoic acid in whale blubber oil; since then it has been noted in various other oils of marine animal origin, including shark liver oil (224), Antarctic whale oil (225), eel oil (226), and turtle oil (227).

In 1924, Grün (214) suggested that a tetradecenoic acid was present in milk fats and Bosworth and Brown (189) found that it constituted about 1% of the total fatty acids of butterfat. Other investigators (228) proved that the acid was 9-tetradecenoic. Concurrent with these investigations others demonstrated the presence of the acid in goat milk fat (192), human milk fat (229), and various animal depot fats (230). Hansen and Shorland (217) have published data on the seasonal variation in the composition of the fatty acids, including tetradecenoic acid, of New Zealand butter.

A tetradecenoic acid was reported by Brooker and Shorland (231) to constitute 0.5% of the fatty acids of the total fatty tissue of the sheep. Shorland (232) reported data on the fatty acid composition of the fats of various grass-fed animals of New Zealand, all of which contained a

tetradecenoic acid as follows: abdominal fat of wild rabbit, 0.4%; total fatty tissue of the horse, 1.4%; perinephric fat of the deer, 0.2%; caul and kidney fat of the ox, 0.3%. The leaf glycerides of the principal grass (rye grass) in the diet of these animals was found to contain 0.2% dodecenoic acid and 0.5% of a tetradecenoic acid. The same author (233) reported that the egg lipids of the hen contained 0.3% of a tetradecenoic acid.

9-Tetradecenoic acid has also been reported to occur in Japanese coccid wax (213); according to Atherton and Meara (234) it constitutes nearly 25% of the total fatty acids of the seed fat of *Pycanthus Kombo* (Kombo nut oil) of Sierra Leone.

Both the natural *cis*-9-tetradecenoic acid (m.p. -4° C.) and *trans*-9-tetradecenoic (m.p. 18.5° C.) have been synthesized by the malonic ester (acyloin) reaction (235).

Pentadecenoic Acids, $C_{15}H_{28}O_2$. Only three of the thirteen possible position isomers of pentadecenoic acid are known, two as the result of synthesis and one from a natural source.

2-Pentadecenoic acid, $CH_3(CH_2)_{11}CH:CHCOOH$, was prepared by Lauer *et al.* (236) by converting myristic acid to the α -hydroxy acid and treating the latter with lead tetraacetate to give tridecanal, $CH_3(CH_2)_{11}CHO$. The aldehyde was then reacted with malonic acid in the presence of pyridine to obtain 2-pentadecenoic acid. The amide melts at 111.5 – 112.5° and the *p*-bromoanilide at 114 – 114.5° C.

6-Pentadecenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_4COOH$, has been reported to be present in human hair fat (16). The acid was identified by oxidizing it to *cis*-dihydroxypentadecanoic acid with 30% hydrogen peroxide in anhydrous formic acid. Two forms of the hydroxyl acid were obtained, one melting at 109.5 – 110° and the other at 82.8 – 83.1° C. The dihydroxy acids were further oxidized with potassium permanganate in boiling acetone to yield *n*-nonanoic acid.

14-Pentadecenoic acid, $CH_2:CH(CH_2)_{12}COOH$, was prepared by Chuit *et al.* (237) by reacting 1-bromo-12-tridecene with diethyl malonate in the presence of sodium ethylate. The acid boils at 195° C. at 8 mm.

Hexadecenoic Acids, $C_{16}H_{30}O_2$. Several hexadecenoic acids bearing names such as hypogeic, palmitoleic, zoömaric, and physetoleic acid, have been reported to occur in various fats and oils. Each of these acids when isolated in sufficient quantity to permit its identification by unequivocal means has been found to be 9-hexadecenoic acid. An exception to this statement is the isolation by Weitkamp *et al.* (16) of a hexadecenoic acid from human hair fat which was identified as 6-hexadecenoic acid. Several hexadecenoic acids have been synthesized, including *cis*-9-hexadecenoic acid (m.p. 0.5° C.) and *trans*-9-hexadecenoic acid (m.p. 31 – 32° C.).

2-Hexadecenoic acid, $\text{CH}_3(\text{CH}_2)_{12}\text{CH}:\text{CHCOOH}$, was prepared by Ponzio (238) by the action of alcoholic potassium hydroxide on 2-iodopalmitic acid. The acid melted at 45°C .

6-Hexadecenoic acid, $\text{CH}_3(\text{CH}_2)_8\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$, was isolated by Weitkamp *et al.* (16) from human hair fat. The purified acid which melted at $9\text{--}10^\circ\text{C}$. was oxidized with 30% hydrogen peroxide in anhydrous formic acid solution to yield the high-melting ($110.5\text{--}111.0^\circ\text{C}$.) and the low-melting ($91\text{--}91.5^\circ\text{C}$.) forms of 6,7-*cis*-dihydroxypalmitic acid. The hydroxy acids were further oxidized with potassium permanganate in boiling acetone to yield *n*-capric acid. The latter melted at 30°C . and gave no depression in melting point when mixed with authentic *n*-capric acid. The same acid has also been reported by Sheng-Lieh Liu (238a) to occur in human hair of males and females.

7-Hexadecenoic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$, was obtained by Marasse (239) and by Bodenstein (240) by fusing stearolic acid, $\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_2)_7\text{COOH}$, with potassium hydroxide. The acid was reported to melt at 21°C .

Another synthetic 7-hexadecenoic acid has been described which melts at 33°C ., boils at 236°C . at 15 mm. pressure, is insoluble in water, soluble in diethyl ether, and very soluble in ethanol. The acid has been called hypogeic acid because of its similarity to an acid by this name and properties (m.p. $34\text{--}35^\circ\text{C}$.) which had been described by Grössmann *et al.* (241) and by Schröder (242) as a constituent of peanut oil, but which Hilditch and Vidyarthi (243) claim is nonexistent.

9-Hexadecenoic (physetoleic, zoömaric) acid, $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, is often referred to as palmitoleic acid because of its structural relationships to palmitic and oleic acids. It is almost as widely distributed in nature as oleic acid, but generally in much smaller amounts. Palmitoleic acid appears to be a component of the lipids of almost all orders of plant and animal life from the highest to the lowest form. It has been found in marine algae (244); diatoms and zoöplankton (245); bacteria (246); yeast (247); cryptogamous spores (248); depot fats of amphibia (249) and reptiles (250); marine animal oils including those derived from rays and sharks (251), humpback (252), sei (253), sperm (254), and other whales (233), porpoise blubber (255), seal oil (256), fish liver oils (257); depot fats of rats (258) and birds (259); the liver glycerides, liver phosphatides, and depot fats of the ox, sheep, pig (260), wild rabbit, and deer (232); milk fats of the cow (261), human (261a), and goat (192); butterfat (262); egg yolk lipids (263); seed and pulp fats of tung and flaxseed (264), teaseed and olive (265), peanut (266), cottonseed, soybean, and oilpalm (267), and milkweed seed (267a).

9-Hexadecenoic acid was first isolated by Hofstädter (254) in 1854 from the head oil of the sperm whale (*Physeter macrocephalus*) and was named physetoleic acid. In 1898, the same acid was isolated by Ljubarsky (256) from seal oil, and in 1906 by Bull (257) from codliver oil. In 1925 its structure was established as 9-hexadecenoic acid by Armstrong and Hilditch (268) who isolated the acid from a South Antarctic whale oil. The methyl ester of the acid was oxidized with powdered potassium permanganate in acetone solution which yielded *n*-heptanoic acid, $\text{CH}_3(\text{CH}_2)_5\text{COOH}$, and azelaic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOH}$. In 1927 this structure was verified by Toyama (253) who subjected the acid obtained from whale and cod liver oils to oxidative fission and likewise obtained *n*-heptanoic and azelaic acids.

cis-9-Hexadecenoic acid and the corresponding *trans*-acid have been synthesized by the malonic ester method (269). The former melts at 0.5° C. and the latter at 31–32° C. Treatment of the *cis*-acid with selenium or the oxides of nitrogen yields an equilibrium mixture of the *cis*- and *trans*-isomers. Oxidation of the *cis*-acid with peracetic acid gives the low-melting form (87° C.) of 9,10-dihydroxypalmitic acid and with alkaline potassium permanganate the high-melting (129–130° C.) stereoisomer. *cis*-9-Hexadecenoic acid was also synthesized by Gupta *et al.* (269a) by the alkyl acetylene method.

The following figures provide an approximate idea of the quantitative occurrence of palmitoleic in nature. The oil extracted from the spores of the so-called "ground pine" (*Lycopodium clavatum*) contains 35% of this acid; the seed fat of the Australian tree, *Macadamia ternifolia*, 20% (270), and the lipids of the marine algae, *Cystophyllum hakodatense*, approximately 20% (244). The fat collected from pelts of ranch-grown mink has been reported (270a) to contain 22.2% hexadecenoic acid. Marine animal oils usually contain 15–20% of 9-hexadecenoic acid; fish oils and the depot fats of amphibia and reptiles, 8–15%; depot fats of rodents and birds, 6–8%. The larger mammals (ox, sheep, and pig) contain 6–8% palmitoleic acid in the liver glycerides and it comprises about 5% of the fatty acids of the liver phosphatides of these animals. The depot fats of these animals contain 2–3% of palmitoleic acid while those of the chimpanzee, tiger, and puma contain 5–6% (271), the horse (total fatty tissue), 6.4% (272). Milk fats and butterfat contain 2–6% of palmitoleic acid (262).

It was formerly assumed that seed and pulp oils contained less than 2% of palmitoleic acid and, except for olive (1.6%) and soybean (ca. 1.2%) oils, generally less than 1%. More recent investigations have revealed

that a number of seed and pulp oils contain appreciably higher amounts of this acid. For example, Hatt and Szumer (273) have reported the seed oil of Kerguelen cabbage (*Pringlea antiscorbutica*) contains up to 4% of palmitoleic acid; Pathak and Mathur (274) found the nut oil of *Areca catechu* contained 7.2% of this acid; and at least one variety of Argentine-grown avocado has been reported (275) to contain 8.3%. The leaf glycerides of rye grass have been found (232) to contain more than 4% of this hexadecenoic acid, and milkweed seed oil 10% (267a).

Heptadecenoic Acids, $C_{17}H_{32}O_2$. Three isomeric heptadecenoic acids have been reported to occur in natural fats and one isomer has been synthesized.

2-Heptadecenoic acid, $CH_3(CH_2)_{13}CH:CHCOOH$, has been synthesized (236) by reacting pentadecanal, $CH_3(CH_2)_{13}CHO$, and malonic acid in the presence of pyridine. The acid melts at $57.5^\circ C$. and its *p*-bromoanilide at $115\text{--}116^\circ C$.

6-Heptadecenoic acid, $CH_3(CH_2)_9CH:CH(CH_2)_4COOH$, was isolated (16) in crude form from human hair fat and oxidized with 30% hydrogen peroxide in anhydrous formic acid which gave a mixture of the high-melting ($111.7\text{--}112.5^\circ C$.) and the low-melting ($88.9\text{--}89.5^\circ C$.) forms of *cis*-6,7-dihydroxyheptadecanoic acid. Further oxidation of the dihydroxy acids with potassium permanganate in boiling acetone gave *n*-hendecanoic acid, $CH_3(CH_2)_9COOH$. The original crude acid consisted of a mixture of 80% 6-heptadecenoic acid and 20% 8-heptadecenoic acid.

8-Heptadecenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_6COOH$, was isolated from human hair fat, as mentioned above, and identified in the same manner (16). Complete fission of the acid gave *n*-nonanoic acid.

9-Heptadecenoic acid, $CH_3(CH_2)_6CH:CH(CH_2)_7COOH$, was isolated by Shorland and Jessop (276) from the mixed fatty acids obtained by saponification of lamb caul fat. Hydrogenation of the unsaturated acid yielded margaric acid, $CH_3(CH_2)_{15}COOH$, and oxidation with powdered potassium permanganate in acetic acid at $50^\circ C$. gave azelaic acid melting at $103\text{--}104^\circ C$. *cis*-9-Heptadecenoic and *n*-heptadecanoic acids were found (276a) to constitute 0.9% and 1.7%, respectively, of the body fat of the Canadian musk ox, *Ovibos moschatus* subsp.

Octadecenoic Acids, $C_{18}H_{34}O_2$. Seventeen position isomers of octadecenoic acid are possible of existence and sixteen of these can exist in two isomeric forms. At least five and possibly more of the position isomers occur in natural fats and oils, and one of these occurs in both the *cis*- and *trans*-form. Six of them have been detected in both the *cis*- and *trans*-form as artifacts produced by the hydrogenation of various unsatu-

rated acids, esters, and glycerides. All but a few of the thirty-three positional and geometric isomers of octadecenoic acid have been synthesized; some of them by several different methods.

This group contains oleic (9-octadecenoic) acid, probably the most prevalent of the natural fatty acids. The early date (1815) of the discovery of this acid and its widespread occurrence stimulated a vast amount of research on the whole series of octadecenoic acids; consequently our knowledge of these acids is more profound than any other related group of monoalkenoic acids.

Another isomer, namely, 6-octadecenoic (petroselinic) acid, has been found to occur in many natural fats and oils, especially in the seed oils of the Umbelliferae, Araliaceae, and Simarubaceae, in human hair fat, and elsewhere. 8-Octadecenoic acid has been detected in human hair fat, olive oil, and elsewhere. 10-Octadecenoic acid has been reported to be present in the body fats of the ox and sheep and in pork liver lipids. Both the *cis*- and *trans*-forms of 11-octadecenoic acids have been found in a number of animal fats.

2-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}:\text{CHCOOH}$, has not been found as a constituent of natural fats but has been synthesized by several methods. In 1904, Ponzio (277) and Le Sueur (278) obtained this acid by the action of alcoholic potassium hydroxide on 2-iodostearic and 2-bromostearic acids, respectively. The position of the double bond was determined by oxidation of the acid to palmitic acid, but its geometric configuration was not determined. The acid was reported to melt at 59°C .

2-Octadecenoic acid has also been prepared by the decomposition of 2-hydroxystearic acid and by fusion of oleic acid with potassium hydroxide (279). The structure of these synthetic acids was investigated by Semeria (280) who concluded that they possessed *trans*-configurations.

More recently *cis*-2- and *trans*-2-octadecenoic acids were prepared by Myers (280a) who also established their structures and those of the related epoxy-, dihydroxy- and dibromoacetoxystearic acids. *cis*-2-Octadecenoic acid melted at 50.5°C . and *trans*-2-octadecenoic acid at 58.5°C . It may therefore be concluded that the acids prepared by Ponzio and by Le Sueur were *trans*-forms.

3-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_{13}\text{CH}:\text{CHCH}_2\text{COOH}$, was first synthesized by Eckert and Halla (282) in 1913 by the action of alcoholic potassium hydroxide on 3-iodostearic acid. The melting point of the acid was reported to be $56\text{--}57^\circ\text{C}$., but its configuration is unknown.

4-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_{12}\text{CH}:\text{CH}(\text{CH}_2)_2\text{COOH}$, was obtained by Eckert and Halla (282) along with 2-octadecenoic acid by the action

of alcoholic potassium hydroxide on 3-iodostearic acid. The position of the double bond of this acid, which melted at 52.5° C., was established by oxidizing it to myristic acid. Its geometric configuration was not established.

5-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_{11}\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$, was obtained by Posternak (283) by the addition of hydrogen iodide to 5-stearolic acid followed by reduction of the addition product with zinc and acetic acid. The acid, which melted at 47.5° C., was believed to be the *trans*-isomer. An acid melting at $42\text{--}43^{\circ}$ C. was obtained by Egorov (284) by fusion of oleic acid with potassium hydroxide. It has been postulated that the latter acid may have had a *cis*-configuration, but the geometric forms of neither acid were established.

cis-6-Octadecenoic (petroselinic) acid, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$, was first isolated by Vongerichten and Köhler (285) from parsley (*Petroselinum sativum*) seed oil, hence the common name of the acid. It is the predominant constituent (ca. 75%) of this and other seed oils of the Umbelliferae family (286). It has also been found in the seed oils of the Araliaceae (287), and in the seed fat of *Picrasma quassioides* (Simarubaceae family) (288), and in human hair fat (16).

The physical properties reported for this acid are not very consistent, probably because it was isolated in different degrees of purity from various sources and synthesized by different methods. Melting points from 29° to 34° C. have been reported. Usually the higher melting points (32° to 34° C.) have been reported for the acid isolated from natural sources, and the lower values (29° to 30° C.) have been reported for the synthetic acid. Similar differences have been noted in the values reported for the density and refractive index of the acid.

The position of the double bond in the natural acid has been established by ozonolysis and oxidation with potassium permanganate in acetone solution.

Petroselinic acid has been prepared synthetically by partial reduction of natural tairic (6-octadecynoic) acid and tairic acid synthesized by two different methods (289,290).

trans-6-Octadecenoic (petroselaidic) acid (m.p. 54° C.) is formed to the extent of 60–65% of the equilibrium mixture when the corresponding *cis*-acid is treated with oxides of nitrogen, selenium, or other isomerizing agent.

Kurono *et al.* (290a) reported that petroselaidic acid was a normal constituent of the oil obtained from the fruits of *Anthriscus sylvestris*, but only in small amounts. These authors also reported that irradiation with

ultraviolet light of plants containing petroselinic acid resulted in the production of petroselaidic acid.

cis-7-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_9\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$ (m.p. 14°C .), and all of the other positional *cis*-isomers up to *cis*-12-octadecenoic acid were prepared by Huber (291) using the alkyl acetylene method of Ahmed and Strong (281). The same acid was also synthesized by Fusari *et al.* (291a) using the same method.

trans-7-Octadecenoic acid was first prepared by Posternak (292) in 1916 by the addition of hydrogen iodide to 7-stearolic acid followed by reduction of the addition product with zinc and acetic acid. He reported the acid to melt at 45.5°C ., which is in good agreement with the melting point (44.5°C .) noted by Huber (291) who obtained the acid by isomerizing with selenium the *cis*-acid prepared as described above.

cis-7- and *trans*-7-Octadecenoic acids were observed by Allen and Kiess (292a) to be formed, among other products, during partial hydrogenation of oleic and elaidic acids and methyl oleate. The *cis*- and *trans*-isomers were formed in the equilibrium ratio of 1:2.

cis-8-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_8\text{CH}:\text{CH}(\text{CH}_2)_6\text{COOH}$, has been reported to occur in human hair fat (16) and olive oil (292a), and its presence in other fats and oils has been suspected.

Arnaud and Posternak (293) claimed to have obtained 8-octadecenoic acid by the action of alcoholic potassium hydroxide on 9-iodostearic acid and also by dehydration of 10-hydroxystearic acid (294). Vanin and Chernoyarova (295) and Pigulevskii and Simonova (296) obtained by different methods an acid melting at 52°C . which they believed to be 7-octadecenoic acid. *cis*-7-Octadecenoic acid, synthesized by unequivocal methods, melts at 24°C . and the corresponding *trans*-isomer at 44°C . *trans*-8-Octadecenoic acid prepared by the same unequivocal method melts at 52.5°C . and it appears that the aforementioned authors may have obtained this isomer rather than the 7-isomer.

Huber (291) synthesized *cis*-8-octadecenoic acid (m.p. 23°C .) by the alkyl acetylene method and from it prepared the *trans*-isomer (m.p. 52.5°C .) by isomerizing the former with selenium. The same two isomers were also prepared by Fusari *et al.* (291a) using the same methods as were applied by Huber.

Many investigators, particularly Allen and Kiess (292a), have shown that partial catalytic hydrogenation of oleic and elaidic acids and their esters produces some shifting of the double bond of these substances to the 8- and 10-position. Allen and Kiess found that during catalytic reduction of oleic and elaidic acid and methyl oleate equal amounts of 8-

and 10-octadecenoates are formed. Both of the positional isomers were found to consist of 1:2 equilibrium mixtures of *cis*- and *trans*-isomers.

cis-9-Octadecenoic (oleic) acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, is generally considered to be the predominant fatty acid in nature. It comprises 50% or more of the total acids of many fats; few fats are known to contain less than 10% of this acid. Oleic acid was first obtained by Chevreul (297) in 1815, but probably not in pure form. In fact, it is unlikely that it was obtained in anything approaching pure form until the modern techniques of isolating and purifying fatty acids were developed; hence many of the physical constants assigned to it in the past cannot always be relied upon.

Where other monoalkenoic acids are present in a natural fat it is unlikely that even the most refined methods permit the isolation of rigidly pure *cis*-9-octadecenoic acid. As more refined methods of examining natural fats have been applied, it has become increasingly apparent that many and perhaps most natural fats contain positionally isomeric oleic acids. Until recently it was believed that olive oil afforded a relatively good source of oleic acid because of its freedom from other isomers. Allen and Kiess (292a), however, reported in 1955 that oleic acid prepared from olive oil varied from 84 to 98% in *cis*-9-octadecenoic acid, the remaining octadecenoic acids consisting of equal amounts of 8- and 10-octadecenoic acids. It is not known with certainty whether this variation in the amount of isomeric oleic acids resulted entirely from shifts in the double bond during isolation of the acid, or partly to this cause and partly to the presence of natural isomers in the oil. It was noted that the purest product (98%) was obtained when the oil was saponified with 3% potassium hydroxide solution.

The position of the double bond in oleic acid was first established by Baruch (299) in 1894 by means of a series of complicated but well-established reactions. The structure assigned to it was subsequently verified by other workers (300) using simpler and more direct methods. Its geometric configuration, namely, the *cis*-form, has been established by a number of investigators (301) and by means of several different methods. Both the position of the double bond and the geometric configuration of oleic acid have been confirmed by several different partial and complete syntheses (302).

trans-9-Octadecenoic (elaidic) acid was first obtained by Poutet (303) in the form of trielaidin in 1819 by treatment of triolein with the oxides of nitrogen derived from mercurous nitrate. Poutet noted that treatment of olive oil, which usually contains 80–85% of oleic acid and about 50% of

the total glycerides in the form of triolein, could be converted to the consistency of pork lard by treatment with mercurous nitrate.

Saytzeff (304) found that the same change occurred when oleic acid was treated with sulfurous acid and sodium bisulfate under pressure and at elevated temperature (180–200° C.). Albitsky (305) found that the reaction was reversible under the same conditions. Rankoff (306) reported that small amounts of sulfur effected a partial conversion of oleic to elaidic acid at 200° C. Griffiths and Hilditch (307) studied the quantitative conversion of oleic to elaidic acid under the influence of several catalysts and also the reverse reaction under identical conditions. They found that the reaction came to equilibrium when the ratio of oleic to elaidic acid was 1:2 regardless of the direction in which the reaction proceeded.

Waterman *et al.* (308) investigated the equilibrium reaction when sulfur dioxide was employed as catalyst under different conditions of temperature and pressure. About the same time Bertram (309) reported that the most efficient reagent for producing the inversion was selenium in concentrations of 0.1–0.3% at 180–200° C.

trans-9-Octadecenoic acid, until recently, was known only as an isomerization product of oleic acid. In 1952, Swern *et al.* (310) demonstrated by infrared analysis that freshly rendered beef fat, edible oleo oil, and oleo stearine contained substantial quantities (5–10%) of *trans*-acids, principally elaidic and vaccenic. Both acids were isolated from oleo oil, elaidic acid apparently for the first time. Subsequently, Hartman *et al.* (311), also by means of infrared spectroscopy, found that *trans*-acids were confined principally to the fats of ruminants (beef cattle, sheep, deer, etc.) and that lard contained only traces of such acids. Elaidic acid has been synthesized by most of the methods mentioned above for the synthesis of oleic acid.

Subbaram and Mahadevan (311a) separated the iso-oleic acids from beef body fat and cow butterfat, oxidized them by the method of Haverkamp-Begemann *et al.* (311b), and analyzed the mixture of dibasic acids by partition chromatography (311c). On the basis of these analyses it was calculated that the original iso-oleic acids from the body fat and butterfat were composed of the following octadecenoic acids: 13-octadecenoic, 23.7 and 20.5%; 12-octadecenoic, 5.1 and tr.; 11-octadecenoic, 26.6 and 49.3%; 10-octadecenoic, 6.9 and tr.; 9-octadecenoic, 29.5 and 17.4%; 8-octadecenoic, 8.3 and 0%, respectively.

10-Octadecenoic acid, $\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$, has been described by a number of workers who obtained it by several different

methods. Saytzeff (279) claimed that he obtained the acid by the action of alcoholic potassium hydroxide on 10-iodostearic acid and by distillation of 10-hydroxystearic acid. Other investigators (312) claim that the dehydration of 10-hydroxystearic acid leads to a mixture of *cis* and *trans* isomers. Baur and Panagoulas (313) claimed that 10-octadecenoic acid is obtained when oleic acid is treated with zinc chloride; while Vanin and Chernoyarova (295) claimed that heating 10-chlorostearic acid with nickel carbonate gave the same acid.

The properties ascribed to these preparations, especially the melting point (44° – 45° C.), would indicate that they were not homogeneous products but rather mixtures of *cis*- and *trans*-isomers and perhaps other products. The melting points of *cis*-10- and *trans*-10-octadecenoic acids synthesized by unequivocal methods are 22.5° and 52.5° C., respectively. Both acids have been synthesized by Huber (291) by the alkyl acetylene method of Strong *et al.* (281).

Gupta *et al.* (314) reported the presence of *trans*-10-octadecenoic acid in the body fats of the ox and sheep, and Channon *et al.* (314a) reported its presence in pork liver lipids. The *trans*-isomer is produced during partial hydrogenation of oleic, linoleic, and eleostearic acids and their esters (315).

11-Octadecenoic acids, $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$, have been found in a number of natural fats and they have been synthesized by several different methods. The early preparations of these acids are of dubious authenticity judging by the properties reported for them. Fokin (316) obtained what he believed to be *cis*-11-octadecenoic acid, together with 12-octadecenoic acid, by dehydrohalogenation of 12-bromostearic acid with alcoholic potassium hydroxide, and also by dehydration of 12-hydroxystearic acid with phosphoric anhydride. The 12-hydroxystearic acid was obtained by hydrogenation of ricinoleic acid in the presence of platinum and the 12-bromostearic acid was prepared from the hydroxy acid. The melting point reported for *cis*-11-octadecenoic acid was 6 – 8° C.

Subsequently, Grün and Czerny (317) investigated the dehydration of 12-hydroxystearic acid and concluded that the reaction lead to a mixture of *cis*-11- and *trans*-11-octadecenoic acids. They reported that the *cis*-isomer melted at 9.8 – 10.4° and the *trans*-isomer at 39.5° C.

Since none of these melting points corresponds to the melting point reported for either the *cis*-isomer (14.5° C.) or the *trans*-isomer (44° C.), synthesized by unequivocal methods (291,291a), it may be concluded that the preparations described above were probably mixtures of *cis*- and *trans*-isomers.

Various investigators (314,315,318,319) have reported the formation of *cis*-11- and *trans*-11-octadecenoic acids during the partial hydrogenation of oleic, linoleic, and eleostearic acids and their esters.

Morton and Todd (320) isolated in small quantity *cis*-11-octadecenoic acid from the lipids of brain tissue. Hofman *et al.* (321) observed its presence in the lipids of *Lactobacillus arabinosus*. The presence of a 11-octadecenoic acid in whale oil has been suggested (322). It forms 15% of the total fatty acids of milkweed seed oil (267a).

trans-11-Octadecenoic (vaccenic) acid has been found in a number of animal fats and oils. It was first isolated by Bertram (323) in 1928 who found it to form about one per cent of the fatty acids of beef fat and 0.01% of the fatty acids of butter fats. Grossfeld and Simmer (324) reported the acid to be present to the extent of 1–2% in mutton fat, 1.6% in beef fat, 0.2% in pork fat, and 1.0–4.7% in butter. Baldwin and Parks (324a) reported the presence of vaccenic acid in the body oil of menhaden (*Brevoortia tyrannus*). Geyer *et al.* (325) reported that the acid was present in pork lard only in traces. Swern *et al.* (310) reported that beef fats contained 5–10% of elaidic and vaccenic acids. Cornwell *et al.* (326) have shown that similar quantities of *trans*-acids are present in butterfat, principally as monene.

cis-11- and *trans*-11-Octadecenoic acids have been synthesized by several different methods. Strong and co-workers (281) and Fusari *et al.* (291a) synthesized these acids by the alkyl acetylene method; Gensler *et al.* (327) by the Grignard reaction using methyl 12-dodecenoate and magnesium butyl bromide; van Loon and van der Linden (328) by the malonic ester method from 9-hexadecenoic acid via 9-hexadecenyl bromide; and Linstead and co-workers (329) by the method of anodic coupling. The *trans*-acid can be prepared from the *cis*-acid by isomerization with selenium which gives the usual equilibrium mixture of the two isomers in the ratio of 1:2 (*cis:trans*).

Shorland *et al.* (329a) incubated oleic, linoleic, and linolenic acids at 37° C. for two days at a controlled pH (6.5–5.8) with an extract of the microorganisms from the rumen of the sheep. They found that in each case considerable hydrogenation occurred with the formation of stearic acid and also *trans*- and positional isomers of the unsaturated acids. In the experiment with linolenic acid, 67% was hydrogenated to *trans*-monenes composed of *trans*-11-, *trans*-12, and *trans*-13-octadecenoic acids.

12-Octadecenoic acids, $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CH}(\text{CH}_2)_{10}\text{COOH}$, have not been found in natural fats, but are produced as artifacts during partial hydrogenation of oils containing linoleic and eleostearic acids.

Fokin (330) claimed that 12-octadecenoic and 11-octadecenoic acids were produced by the action of alcoholic potassium hydroxide on 12-bromostearic acid, and by the dehydration of 12-hydroxystearic with phosphoric anhydride. The melting point of 12-octadecenoic acid prepared by these means was reported to be 33–34° C., whereas the melting points of the *cis*- and *trans*-isomers synthesized by unequivocal methods are 27.5° and 52.5° C., respectively. Fokin's preparations appear to be a mixture of these two isomers and possibly other positional isomers.

cis-12- and *trans*-12-Octadecenoic acids have been synthesized by Huber (291) by the alkyl acetylene method (281). Various workers (315,331) have reported the formation of one or both of these isomers during partial hydrogenation of linoleic and eleostearic acids and oils containing these acids.

13-Octadecenoic acids, $\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOH}$, have been found by Allen and Kiess (332) to be formed together with other positional isomers when methyl eleostearate is partially hydrogenated. They found that the stepwise addition of 2 moles of hydrogen to methyl eleostearate, either in the presence or absence of solvent, led to the formation of equimolar quantities of 9-, 10-, 11-, 12- and 13-octadecenoates. Both *cis*- and *trans*-isomers of each positional isomer were formed during the hydrogenation.

15-Octadecenoic acid, $\text{CH}_3\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_{13}\text{COOH}$, was reported by Bauer and Ermann (333) to be formed by the partial hydrogenation of linolenic acid.

17-Octadecenoic acid, $\text{CH}_3\text{CH}:\text{CH}(\text{CH}_2)_{14}\text{COOH}$, has been synthesized by Huber (291) starting with ethyl 10-henecenoate which was reduced with lithium aluminum hydride to 10-hendecenol. The unsaturated alcohol was converted to the bromide by treatment with phosphorus tribromide. The Grignard compound of the bromide was treated with cadmium chloride and the product reacted with 6-carbethoxycaproyl chloride to yield ethyl 7-keto-17-octadecenoate. Hydrolysis and reduction with hydrazine of the last-mentioned product yielded 17-octadecenoic acid.

Gupta (333a) also prepared 17-octadecenoic acid from ω -hydroxystearic acid obtained from kamala seed oil. The hydroxy acid was converted to the corresponding ω -chlorostearic acid by treatment with thionyl chloride. The chloro acid was heated with 25% alcoholic potassium hydroxide solution to dehydrohalogenate it. The 17-octadecenoic acid thus obtained was crystallized from dilute methanol. The acid melted at 55.0–55.5° C. and on complete hydrogenation in alcoholic solution with a platinum catalyst it gave stearic acid.

Nonadecenoic Acids, $C_{19}H_{36}O_2$. No nonadecenoic acids have been observed to occur in natural fats. The preparation of 2-nonadecenoic acid, $CH_3(CH_2)_{15}CH:CHCOOH$, was described by Oskerk (334), who obtained it by dehydrohalogenation of 2-bromononadecanoic acid which in turn was prepared by the action of bromine and phosphorus on nonadecanoic acid.

Eicosenoic Acids, $C_{20}H_{38}O_2$. Two positionally isomeric eicosenoic acids, namely, *cis*-9-eicosenoic (gadoleic) acid and *cis*-11-eicosenoic (gondoic) acid have been isolated from natural fats. Both the *cis*- and *trans*-forms of gadoleic acid have been synthesized by at least two different methods.

cis-9-Eicosenoic (gadoleic) acid, $CH_3(CH_2)_9CH:CH(CH_2)_7COOH$, has been found to be widely distributed in fish and marine mammalian oils, but it generally forms only 5 to 15% of the total fatty acids. The acid was first isolated by Bull (335) in 1906 from codliver oil. The acid was named gadoleic from the generic name of the cod, *Gadus*. In 1918, Lexow (209) reported that herring oil contained 11.7% of this acid, and subsequently Toyama and co-workers (336) reported its presence in shark and ray liver oils and in whale oil. Hilditch and Houlbrooke (337) found that it constituted 16.4% of the fatty acids of shark liver oil.

The structure of gadoleic acid isolated from sardine oil was established by Takano (338) in 1933 and was later verified by Toyama and Tsuchiya (339) who isolated it from codliver, herring, and whale oils. This structure was verified in 1949 by Bowman (340) who synthesized *cis*-9- and *trans*-9-eicosenoic acid by the malonic ester (acyloin) method. In 1953, Gupta *et al.* (269a) reported the synthesis of *cis*-9-eicosenoic acid, as well as *cis*-9-hexadecenoic and 12,16-tetracosenoic acid by the alkyl acetylene method.

11-Eicosenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_9COOH$, appears to have been noted first by Toyama and Ishikawa (341) in 1934 as a constituent of pilot whale oil, although they reported it simply as an isomer of gadoleic acid and called it gondoic acid. Baldwin and Parks (324a), however, reported the presence of 11-eicosenoic acid in menhaden oil in 1943. Subsequently, the same acid was observed by Hopkins *et al.* (342) to be present in Atlantic cod oil. Later, they reported that it comprised 11 and 4%, respectively, of the fatty acids of dogfish liver oil (*Squalus acanthias* L.) and of the blubber oil of the beluga or white whale, *Delphinapterus leucas* (Pallas).

The acid was first reported to be a constituent of plants by Greene and Foster (343) who noted its presence in the seed lipids of the California

jojoba shrub, *Simmondsia chinensis* (California), of the Buxaceae family. The clear light yellow liquid obtained by pressing or extracting the seeds of this shrub is a liquid wax and not a glyceride oil. It consists largely of the monoesters of 11-eicosenoic (64.4%) and 13-docosenoic (erucic) (30.2%) acids and 11-eicosenol and 13-docosenol (343,344).

Hopkins and co-workers (345) found the acid to be present in small proportions in the seed oil of *Conringia orientalis* and verified the position of the double bond. Much later (1958) Chisholm and Hopkins (345a) found that 11-eicosenic acid composed 42% of the total fatty acids of the seed oil of the balloon vine, *Cardiospermum halicacabum*. Baliga and Hilditch (346) found the acid to be present in rape and mustard seed oils. Holmberg and Sellman (347) found it in the seed oils of other Cruciferae. Hatt and Szuner (273) reported its presence in the seed oil of Kerguelen cabbage in which it comprised 13.8% of the total fatty acids. Hopkins and Chisholm (348) found it as a constituent of the seed oils of rutabaga (*Brassica napobrassica*) (Mill.) and fenchweed (*Thlaspi arvense* L.).

It is most probable that many of the marine oils which have been reported to contain eicosenoic acid may actually contain a mixture of *cis*-9- and *cis*-11-eicosenoic acids. Partial hydrogenation of these oils would result in some shifting of the double bonds and also the production of *trans*-isomers. They may also result from the partial hydrogenation of more highly saturated marine oils.

Docosenoic Acids, $C_{22}H_{42}O_2$. Two docosenoic acids have been found to be constituents of natural fats, namely, 11-docosenoic (cetoleic) acid, which has been found in many fish and marine mammalian fats, and 13-docosenoic (erucic), which has been found in a large number of seed oils. The latter acid has also been synthesized by several methods.

2-Docosenoic acid, $CH_3(CH_2)_{18}CH:CHCOOH$, prepared by the action of alcoholic potassium hydroxide on iodobehenic acid, was described by Alexandroff and Saytzeff (348a). The acid was reported to melt at 54–58° C. It probably consisted of a mixture of isomers.

cis-11-Docosenoic (cetoleic) acid, $CH_3(CH_2)_9CH:CH(CH_2)_9COOH$, is found in many marine oils, together with gadoleic acid, but usually in smaller proportions than the latter. Toyama (349) was the first to establish the identity of this acid which had previously been believed to be identical with the isomeric erucic acid found in vegetable oils. Cetoleic acid has been found as a component of whale oils (349,350), shark liver oils (337,351), herring oil (352), sardine oil (353), and pin-fish oil (354).

cis-13-Docosenoic (erucic) acid, $CH_3(CH_2)_7CH:CH(CH_2)_{11}COOH$, is the principal constituent of the seed oils of the Cruciferae and Tropaeo-

laceae in which it forms 40 to 80% of the total fatty acids. It was first observed by Darby (355) in 1849 in mustard-seed oil, but its structure was not established until 1893 when Fileti (356) obtained from it non-anoic acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$, and brassylic acid, $\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$, by disruptive oxidation with nitric acid.

Erucic acid was first isolated from rapeseed oil by Websky (357) in 1853 and since then it has been isolated from the same sources by others (358) who found it to comprise 40 to 50% or more of the total fatty acids of this oil. Other cruciferous oils containing this acid are wallflower seed (40.6%) (359), mustard seed (41.5%) (360), and jamba seed (46.3%) (361). Hilditch and Meara (362) found erucic acid to comprise 82% of the total fatty acids of nasturtium seed oil.

Hatt and Szumer (273) reported that the seed fat of Kerguelen cabbage (*Pringlea antiscorbutica*) contained 13% of erucic acid. Hopkins and Chisholm (348) found that the seed oil of fenchweed (*Thlaspi arvense* L.) contained 37% of this acid. An unidentified docosenoic acid, probably erucic, was reported by Alvarez *et al.* (363) to be present in the fat of three varieties of Argentine avocados. Ligthelm *et al.* (364) found 0.2 to 2.3% of erucic acid in the kernel oils of three different species of *Ximenia*.

Erucic acid has been synthesized by Bounds *et al.* (365) from methyl hydrogen adipate, $\text{HOOC}(\text{CH}_2)_4\text{COOCH}_3$, and oleic acid by the method of anodic coupling; also by Bowman (340) by the malonic ester (methoxy-ketone) method.

trans-13-Docosenoic (brassicic) acid has been prepared by many workers (365a) by treating erucic acid with a variety of isomerizing reagents. Brassicic acid has been synthesized by Bowman (340) by the malonic ester (methoxy-ketone) method, and by Bounds *et al.* (365) by the method of anodic coupling of methyl hydrogen adipate and elaidic acid.

Tricosenoic Acids, $\text{C}_{23}\text{H}_{44}\text{O}_2$. No tricosenoic acid appears to have been isolated from a natural fat. One isomer, namely, 22-tricosenoic acid, has been synthesized by Stenhagen (365b) by lengthening the chain of 10-hendecenoic acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_5\text{COOH}$. The latter acid was converted to the chloride by treatment with thionyl chloride and the chloride condensed with ethyl acetoacetate. The condensation product was hydrolyzed to give methyl 3-keto-12-tridecenoate which was alkylated with ethyl 11-iodohendecenoate. The alkylated product was hydrolyzed and cleaved to give 13-keto-22-tricosenoic acid (m.p. 86.5–86.7° C.). The keto acid was reduced by the Huang-Minlon modification of the Wolff-

related C_{24} -acids, namely, lignoceric, $CH_3(CH_2)_{22}COOH$; α -hydroxylignoceric, $CH_3(CH_2)_{21}CHOHCOOH$; nervonic, $CH_3(CH_2)_7CH:CH(CH_2)_{13}COOH$; and α -hydroxynervonic, $CH_3(CH_2)_7CH:CH(CH_2)_{12}CHOHCOOH$.

In 1954, Ligthelm *et al.* (364) reported the presence of 15-tetracosenoic acid in the kernel oils of several species of *Ximenia* in which it comprised 3 to 7% of the total fatty acids.

Shortly after selacholeic acid was isolated from a natural source it was synthesized by Hale *et al.* (370) who condensed 13-docosenyl bromide with ethyl malonate to obtain a mixture of *cis*-15- and *trans*-15-tetracosenoic acids. After separation of the two isomers the *cis*-acid was found to melt at $39^\circ C$. and the *trans*-acid at $61^\circ C$. The two isomers were synthesized independently by Bounds *et al.* (371) by anodic coupling of methyl hydrogen suberate and oleic and elaidic acid, respectively. They reported a melting point of $40\text{--}41^\circ C$. for *cis*-15-tetracosenoic acid and $65.5^\circ C$. for the *trans*-isomer.

Hexacosenoic Acids, $C_{26}H_{50}O_2$. Two isomeric hexacosenoic acids have been found in natural fats, namely, 9-hexacosenoic and 17-hexacosenoic (ximenic). The former has been found only in marine fats and the latter only in plant fats. At least two other hexacosenoic acids have been detected in brain cerebrosides and spingomyelin, but their structures are not known.

9-Hexacosenoic acid, $CH_3(CH_2)_{15}CH:CH(CH_2)_7COOH$, has been reported by Bergmann and Swift (372) to be a component of the lipids derived from the sponge, *Speciospongia vesparia*.

cis-17-Hexacosenoic (ximenic) acid, $CH_3(CH_2)_7CH:CH(CH_2)_{15}COOH$, was first reported in 1937 by Puntambekar and Krishna (373) to be a constituent of the seed oil of the Indian shrub, *Ximenia americana*, family Olacaceae. Two years later it was shown by Boekenoogen (374) to be 17-hexacosenoic acid. Ligthelm *et al.* (364) found ximenic acid to be present in the seed oils of several South African species of *Ximenia*. They reported the acid to comprise 3.5% of the total fatty acids of *X. caffra*, 7.0% of *X. caffra* var. *natalensis*, and 8.7% of *X. americana* var. *microphylla* compared with 14.6 and 25%, respectively, for Indian and West African *X. americana*.

Klenk and Schumann (375) reported the isolation of a hexacosenoic acid (m.p. $45\text{--}45.5^\circ C$.) from brain cerebrosides, but did not determine its structure. The same hexacosenoic acid or an isomer thereof has been reported to comprise 3% of the total fatty acids of spingomyelin.

Octacosenoic Acids, $C_{28}H_{54}O_2$. Two octacosenoic acids have been detected in natural fats; one is 19-octacosenoic acid and the other is of unknown structure.

An octacosenoic acid melting at $57-58^\circ$ C. was reported by Bergmann and Swift (372) to be a component of the lipids extracted from the sponge, *Suberites compacta*. Its structure was not determined.

19-Octacosenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_{17}COOH$, was found by Ligthelm *et al.* (364) to comprise 4.7% to 12.2% of the seed oils of various species of *Ximenia*.

Triaccontenoic Acids, $C_{30}H_{58}O_2$. Boekenoogen (374) reported the presence of 21-triaccontenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_{19}COOH$, which he named lumequeic (lumequic) acid from the African name, lumeque nuts, by which the seeds are known.

Lumequeic acid was found by Ligthelm *et al.* (364) to constitute 3 to 7% of the fatty acids of various African *Ximenia* oils.

Dotriaccontenoic Acids, $C_{32}H_{62}O_2$. Ligthelm *et al.* (364) reported the presence of a dotriaccontenoic acid of undetermined structure in the seed oils of two species of *Ximenia*, namely, *X. caffra* and *X. americana*. The acid was present in both oils to the extent of approximately 1% of the total fatty acids.

(b) Alkadienoic Acids, $C_nH_{2n-4}O_2$

In addition to the large number of monoalkenoic acids there is found in nature and especially in the natural fats several series of polyunsaturated acids containing one to six centers of unsaturation. One series comprises the diunsaturated or alkadienoic acids, also referred to as dienoic, diethenoic, and diolefinic acids. The number of alkadienoic acids known to occur in natural fats is small compared to the number of known monoalkenoic acids and the structures of the former are less diverse than those of the latter.

Except for sorbic acid, which occurs in nature but not as a constituent of natural fats, most of the naturally occurring acids of this group contain 18 or more carbon atoms. The best-known and most widespread of these acids is linoleic, the presence of which in sufficient proportion confers drying properties on an oil. Dienoic acids are found in marine and terrestrial animal oils, but they are predominantly associated with oils of plant origin.

A pair of double bonds of polyunsaturated acids may be attached to (a) the same carbon atom as in 2,3,4-decatrienoic acid, $CH_3(CH_2)_4CH:C:C:CHCOOH$, found in the flowers of *Matricaria inodora*; (b) adjacent

carbon atoms as in sorbic acid, $\text{CH}_3\text{CH}:\text{CHCH}:\text{CHCOOH}$, which is found in unripe sorb apples; or (c) isolated carbon atoms as in linoleic acid, $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, found in linseed oil. Each unconjugated dienoic acid, except those with terminal unsaturation, can exist in four geometric forms, namely, *cis,cis-*, *trans,trans-*, *cis,trans-*, and *trans,cis-*.

In addition to the dienoic acids which have been observed in nature, others have been synthesized by partial or total methods, and a number of others are known as artifacts produced by partial hydrogenation of polyunsaturated acids or oils.

The principal normal alkadienoic acids found in nature are collected in Table 15.

Pentadienoic Acids, $\text{C}_5\text{H}_6\text{O}_2$. The pentadienoic acids are not found as components of natural fats, and only the 2,4-pentadienoic acid is well known.

2,4-Pentadienoic (β -vinylacrylic) acid, $\text{CH}_2:\text{CHCH}:\text{CHOOH}$, was first prepared by Doebner (376) in 1902 from acrolein and malonic acid in the presence of pyridine which is a general method for preparing 2,4-dienoic acids, all of which contain the conjugated carbon system, $-\text{C}:\text{CHCH}:\text{C}-$. These acids do not always exhibit the typical reactions of conjugated acids because they are modified to some extent by the proximity of the terminal carboxyl group.

β -Vinylacrylic acid is a colorless, crystalline solid melting at 80°C . On heating to $110-115^\circ \text{C}$. it undergoes polymerization to a viscous liquid. It is soluble in hot water, slightly soluble in petroleum naphtha, and very soluble in ethanol and diethyl ether.

The acid adds bromine at the terminal double bond to give 4,5-dibromo-2-pentenoic acid, $\text{CH}_2\text{BrCHBrCH}:\text{CHCOOH}$. It adds hypochlorous acid exclusively at the terminal double bond to give $\text{CH}_2\text{ClCHOCH}:\text{CHCOOH}$ in conformance with Markownikoff's rule. Reduction with hydrogen and platinum oxide yields ethyl acrylic (2-pentenoic) acid, $\text{CH}_3\text{CH}_2\text{CH}:\text{CHCOOH}$, whereas reduction with sodium amalgam occurs by 1,4-addition of hydrogen to give principally 3-pentenoic acid, $\text{CH}_3\text{CH}:\text{CHCH}_2\text{COOH}$, with a small amount of vinylpropionic (allylacetic) acid, $\text{CH}_2:\text{CHCH}_2\text{CH}_2\text{COOH}$, by 1,2-addition.

Oxidative fission occurs with potassium permanganate at the 4-position to give formic and tartaric acids. When heated with ammonium hydroxide solution, β -vinylacetic acid adds two moles of ammonia to form 3,5-diaminovaleric acid, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CHNH}_2\text{CH}_2\text{COOH}$.

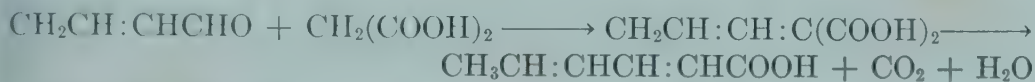
TABLE 15
Alkadienoic Acids $C_nH_{2n-4}O_2$

Systematic name	Common name	Formula, $R-COOH$	Formula weight	M.p., ° C.	B.p., ° C. mm.	Source
2,4-Pentadienoic	β -Vinyl-acrylic	$CH_2:CHCH:CH-$	98.10	80	d. 110	Synthetic
2,4-Hexadienoic	Sorbic	$CH_3CH:CHCH:CH-$	112.12	134.5	d. 228	Mountain ash
2,4-Decadienoic		$CH_3(CH_2)_4CH:CHCH:CH-$	168.23			Stillingia oils
2,4-Dodecadienoic		$CH_3(CH_2)_6CH:CHCH:CH-$	196.28			<i>Sebastiana linguistina</i>
9,12-Octadecadienoic	Linoleic	$CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_7-$	280.44	-5	202/1.4	Plant and animal oils
10,13-Nonadecadienoic		$CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_8-$	294.46			Synthetic
11,14-Eicosadienoic		$CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_9-$	308.49			Shark liver oil
α,γ -Docosadienoic		$CH_3(CH_2)_6CH:CHCH_2CH:CH(CH_2)_x-$	336.54			Brassica oils, etc.
17,20-Hexacosadienoic		$CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_{15}-$	392.64			<i>Speciospongia ves-paria</i>

Hexadienoic Acids, $C_6H_8O_2$. Although several positional and geometric isomers of hexadienoic acid are theoretically possible only the 2,4-hexadienoic acid has been found in nature. For industrial use the acid is produced synthetically as there is no known natural source from which it can be obtained economically and in the required quantities.

2,4-Hexadienoic (sorbic) acid, $CH_3CH:CHCH:CHCOOH$, was first obtained by Hofmann (377) in 1859 from the unripe berries of the mountain ash. It is a colorless, crystalline solid melting at $134.5^\circ C.$, slightly soluble in water (0.2% by weight) and very soluble in ethanol, diethyl ether, and other organic solvents.

The acid is readily prepared in the laboratory by reaction of crotonaldehyde and malonic acid in the presence of pyridine in accordance with the following equation:



Reaction of crotonaldehyde with the zinc derivative of ethyl bromoacetate yields sorbic acid by the Reformatsky reaction. Oxidation of 2,4-hexadienal, $CH_3CH:CHCH:CHCHO$, with silver compounds (378), and oxidation of 3,5-heptadiene-2-one, $CH_3CH:CHCH:CHCOCH_3$, with sodium hypochlorite also yields sorbic acid. Commercially the acid is manufactured by condensing crotonaldehyde and ketene in the presence of a catalyst such as boron fluoride, followed by destructive distillation at reduced pressure (379,380).

The reactions of sorbic acid are similar to those of β -vinylacrylic acid. Partial hydrogenation gives hydrosorbic (3-hexenoic) acid and to a lesser extent 2,3- and 2,4-addition products. Chlorine adds to the terminal double bond to form 4,5-dichloro-2-hexenoic acid, $CH_3CHClCHClCH:-CHCOOH$. Treatment with liquid hydrogen chloride at high temperature and pressure yields 5-chloro-3-hexenoic acid, $CH_3CHClCH:CHCH_2COOH$. Dilute hypochlorous acid yields a mixture of 4-hydroxy-5-chloro-2-hexenoic acid and its lactone (381). One mole of bromine adds to sorbic acid in carbon disulfide or glacial acetic acid solution to give principally crystalline 3,4-dibromohexenoic acid together with a small amount of 1,2-dibromo product (381a). With 2 moles of bromine it forms a tetrabromohexanoic acid.

Disruptive oxidation with potassium permanganate or dichromate occurs at the double bonds while organic peracids (peracetic, perbenzoic) react to give 4,5-epoxy-2-hexanoic acid. Sorbic acid undergoes the Diels-Alder reaction with many compounds. It also undergoes polymerization

without catalysts or prolonged heating, and it copolymerizes with unsaturated monomers, such as vinyls and acrylates.

Sorbic acid is used principally in the manufacture of protective and decorative coatings. Glyceride esters and some of the other esters of sorbic acid exhibit the properties and behavior of animal and vegetable fats. Allyl sorbate and glycol disorbate dry rapidly and form hard films on exposure to air. It is reported that, by means of ester interchange reactions between sorbic acid, glycerol, and linseed oil, products are obtained which are equivalent to those prepared from tung oil; reaction with soybean oil yields products which it is claimed are similar to those produced with dehydrated castor oil; and tung oil itself is said to be improved by modifications of this type (382).

Sorbic acid, its salts, and esters have mold- and yeast-inhibiting properties. It is reported that more than one million pounds annually of sorbic acid is employed in the food industry in the United States, principally as a mold inhibitor. It is normally used in concentrations of less than 0.1%; when used in these low concentrations it will inhibit mold growth but at the same time permit the growth of lactobacilli which are required for proper curing of Cheddar cheese. Similar behavior has been noted when used in curing pickles. It is also reported that sorbic-treated wrappers are used to protect sliced processed cheese, and that it can be incorporated into cake batters to retard mold growth without interfering with cake flavor.

Decadienoic Acids, $C_{10}H_{16}O_2$. Only one decadienoic acid has been found in natural fats, namely, 2,4-decadienoic, $CH_3(CH_2)_4CH:CHCH:-CHCOOH$. It has been found only in stillingia oils derived from the seeds of *Sapium sebiferum* (Chinese tallow tree) and *S. discolor*. This conjugated C_{10} -acid forms 4 to 5% by weight of the total fatty acids of these oils.

The presence of an acid having a characteristic absorption band at about $260\text{ m}\mu$ was first noted in stillingia oil by Potts (383). The acid which gives rise to this absorption was first isolated by Devine (384) who also established its structure. This structure was subsequently confirmed by Hilditch *et al.* (385).

2,4-Decadienoic acid is a liquid at ordinary temperatures and is very susceptible to autoxidation. On complete hydrogenation it yields *n*-decanoic acid and on disruptive oxidation of the methyl ester it yields methyl *n*-hexanoic acid. On partial hydrogenation of the methyl ester it has been found to yield mainly the ester of 3-decenoic acid together with some methyl 2-, and 4-decenoate.

Dodecadienoic Acids, $C_{12}H_{20}O_2$. The presence of 2,4-dodecadienoic acid $CH_3(CH_2)_6CH:CHCH:CHCOOH$, in the seed oil of *Sebastiania linguistrina*, a member of the Euphorbiaceae native to the southern United States, was suggested by Hanks and Potts (386) on the basis of an ultra-violet absorption peak at 268 $m\mu$ and determination of the equivalent weight of the acid. The acid was subsequently isolated by Holman and Hanks (387) by alcoholysis of the oil, fractional distillation of the methyl esters, and displacement chromatography of the C_{12} -fraction. Complete hydrogenation of the unsaturated acid gave lauric acid.

Octadecadienoic Acids, $C_{18}H_{32}O_2$. Until about a decade ago the only well-recognized octadecadienoic acids were natural linoleic and its eladinized product, linolelaidic acid, both 9,12-octadecadienoic acids. Since then the number of known or detected octadecadienoic acids has been appreciably augmented, but by comparison with the total number of possible isomers our knowledge of these acids is still very incomplete. Most of the known isomers have double-bond systems but slightly removed from those of the natural acid. For the most part these isomers have been derived from natural linoleic acid or from other natural acids having unsaturated linkages in the same or contiguous positions, by applying to them such reactions as hydrogenation, alkali isomerization, or dehydration.

Not all of the acids produced by the aforementioned reactions have been isolated and characterized, but evidence for their existence rests on trustworthy methods of detection. Those octadecadienoic acids which have been characterized at least to the extent of melting point determinations have been collected in Table 16.

Linoleic Acid. *cis*-9,*cis*-12-Octadecadienoic (linoleic) acid, $CH_3-(CH_2)_4CH:CHCH_2CH:CH(CH_2)_7COOH$, is widely distributed in the plant kingdom; by frequency and proportionality, it is the most important polyalkenoic acid found in vegetable fats. It is a characteristic and often major component of many of the important fats of commerce, including cottonseed, soybean, peanut, corn, sunflowerseed, poppyseed, linseed, and perilla oils. Linoleic acid is almost invariably accompanied by oleic acid in vegetable oils and it is generally considered characteristic of semidrying and drying oils. However, unless modified in some manner to improve their drying characteristic, vegetable oils containing acids no more unsaturated than linoleic find limited employment in the protective and decorative coating industry. Peanut, palm, teaseed, kapok, and similar oils having less than 25% linoleic acid have no practical value as drying oils. Corn germ, cottonseed, sunflowerseed, poppyseed, sesame,

TABLE 16
 Isomeric Octadecadienoic Acids

Isomer	Source	M.P., ° C.	Authority
<i>cis</i> -9, <i>cis</i> -12	Natural fats	-5.0	Matthews, Brode, and Brown ^a
<i>trans</i> -9, <i>trans</i> -12	Selenium-isomerized linoleic	28-29	Kass and Burr ^b
<i>cis</i> -9, <i>trans</i> -11	Alkali-isomerized linoleic	22-23	Nichols <i>et al.</i> ^c
<i>trans</i> -10, <i>cis</i> -12	Alkali-isomerized linoleic	3	Nichols <i>et al.</i> ^c
<i>cis</i> -9, <i>cis</i> -11	Alkali-isomerized linoleic	19-20	von Mikusch ^d
<i>cis</i> -10, <i>cis</i> -12	Alkali-isomerized linoleic	21-22	von Mikusch ^d
<i>trans</i> -9, <i>trans</i> -12	Alkali-isomerized linoleic	42-43	Ahlers, Brett and McTaggart ^e
<i>trans</i> -10, <i>trans</i> -12	Dehydrated ricinoleic	57	Ahlers <i>et al.</i> , ^e also ^{f,g}
<i>trans</i> -10, <i>trans</i> -12	Alkali-isomerized, dehydrated castor oil acids	57	von Mikusch ^h
<i>trans</i> -9, <i>trans</i> -11	Dehydrated ricinoleic	43	Ahlers <i>et al.</i> , ^e also ⁱ
<i>trans</i> -8, <i>trans</i> -10	Dehydrated ricinoleic	56	Smit and Böeseke ^j von Mikusch ^l
<i>trans</i> -9, <i>trans</i> -11	Debrominated 11-bromooleic	32-33	Schmid and Lehmann ^k
<i>trans</i> -8, <i>trans</i> -10	Debrominated tetrabromide of dehydrated castor oil acids	56	von Mikusch ^l

^a N. L. Matthews, W. R. Brode, and J. B. Brown, *J. Am. Chem. Soc.*, **63**, 1064-1067 (1941).

^b J. P. Kass and G. O. Burr, *J. Am. Chem. Soc.*, **61**, 1062-1066 (1939); T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind. London*, **58**, 233-241 (1939).

^c P. L. Nichols, Jr., S. F. Herb, and R. W. Riemenschneider, *J. Am. Chem. Soc.*, **73**, 247-252 (1951).

^d J. D. von Mikusch, *Ind. vernice Milan*, **6**, 15-22 (1952).

^e N. H. Ahlers, R. A. Brett, and N. G. McTaggart, *J. Appl. Chem.*, **3**, 433-443 (1953).

^f J. D. von Mikusch, *Lack u. Farben Chem.*, **3**, No. 9/10, 167-176 (1949).

^g L. P. Witnauer, P. L. Nichols, Jr., and F. R. Senti, *J. Am. Oil Chemists' Soc.*, **26**, 653-655 (1949).

^h J. D. von Mikusch, *J. Am. Chem. Soc.*, **64**, 1580-1582 (1942).

ⁱ C. Mangold, *Monatsh.*, **15**, 307-315 (1894).

^j W. C. Smit and J. Böeseke, *Rec. trav. chim.*, **49**, 539-551, 686-690 (1930).

^k H. Schmid and A. Lehmann, *Helv. Chim. Acta*, **33**, 1494-1502 (1950).

^l J. D. von Mikusch, *J. Am. Oil Chemists' Soc.*, **29**, 114-115 (1952).

and similar oils containing 40 to 65% and little or no linolenic acid, although classed as semidrying oils likewise find almost no use in the drying oil industry.

Linoleic acid is seldom found in appreciable amounts of terrestrial animal fats unless it is a component of the diet. Normally the linoleic acid content of the fats of land animals constitutes 2 to 14% of the total fatty acids, except that in some birds it may exceed 20%. Although the fats

derived from many marine animals may contain a large proportion of C_{18} -acids, they are generally more unsaturated than linoleic. Japanese sardine oil (*Clupanodon melanostica*) appears to be an exception since it contains about 24% of octadecadienoic acid.

Linoleic acid is a colorless to light-yellow liquid melting at -5 to -5.27°C ., boiling at 202°C . at 1.4 mm. pressure. It is insoluble in water but is miscible in all proportions with methanol, diethyl ether, and most other organic solvents.

Linoleic acid is often referred to as an "essential" fatty acid because many animals, and possibly all of them, lack ability to synthesize it from carbohydrates.

Linoleic (linolic) acid appears to have been described first by Sacc (388) in 1844, who separated it from the mixed fatty acids derived from linseed oil. In 1886, Peters (389) assigned to it the formula $C_{18}H_{32}O_2$. It was thus evident that linoleic contained two double bonds and it could therefore exist in four geometric forms. Many subsequent investigations were directed toward establishing the position and stereochemical configuration of the double bonds of the natural acid.

The early studies directed toward this problem were based largely on the reaction of linoleic acid with bromine and oxidation with alkaline potassium permanganate. The important observations resulting from the study of bromine addition to natural linoleic acid may be summarized as follows:

Bromination of linoleic acid yields two tetrabromostearic acids in almost equal proportion, one a solid melting at 115.5°C . and the other a liquid. This observation led Bedford (390) to infer that the natural acid was composed of two isomers which were designated α -linoleic and the other β -linoleic. However, Rollett (391) demonstrated that α -linoleic acid obtained by regeneration from the solid bromostearic acid gave the same two solid and liquid tetrabromides on rebromination, and concluded that the natural acid consisted of only one isomer which on bromination resulted in the formation of two isomeric addition products. This conclusion was subsequently verified by a number of other workers (392).

Hydroxylation of the double bonds of linoleic acid by alkaline potassium permanganate produces two tetrahydroxystearic (α - and β -sativic) acids in approximately equal amounts. The melting points of the respective acids are 163.5° and 174°C . (393). See Chapter XIII for further discussion of these acids.

The results obtained by applying the aforementioned bromination and oxidation reactions to natural linoleic acid and its elaidinization product

led to the assignment of the complete structure to the natural acid as *cis*-9-,*cis*-12-octadecadienoic acid, and *trans*-9,*trans*-12-octadecadienoic to the eladinization product. These structures were confirmed by infrared (394) and Raman (395) spectral analysis (see Chapter V). The structure of linoleic acid was also confirmed by Arcus and Smedley-Maclean (395a) by means of ozonolysis.

The first synthesis of linoleic acid was reported by Noller and Girvin (396) in 1937. To achieve this synthesis they prepared vinyl *n*-hexylcarbinol, $\text{CH}_3(\text{CH}_2)_4\text{CHOHCH}:\text{CH}_2$, by reacting acrolein with *n*-amyl magnesium bromide, which was then treated with phosphorus tribromide. The product was a mixture of 1-bromo-2-octene and 3-bromo-1-octene. The Grignard reagent was prepared from the mixed bromo-octenes and reacted with 8,9-dibromo-9-methoxynonyl chloride to yield a mixture of the desired linoleic acid and a branched-chain acid. Neither the normal nor the branched-chain acid was isolated in pure form, and no crystalline tetrabromide could be separated after bromination. Hydroxylation, however, yielded a small amount of tetrahydroxystearic acid.

In 1944, Baudart (397) synthesized *trans*-9,*trans*-12-octadecadienoic (linolelaidic) acid starting with glutaric aldehyde, $\text{OHC}(\text{CH}_2)_3\text{CHO}$, and applying a series of chain-lengthening Grignard condensations (magnesium alkyl bromide).

The corresponding *cis*-9,*cis*-12-octadecadienoic (linoleic) acid was first obtained by Raphael and Sondheimer (398) in 1950 by means of the alkyl acetylene synthesis. The following year two further syntheses of the same acid were reported by Walborsky *et al.* (399) and by Gensler and Thomas (400) by somewhat similar methods starting with 1-bromo-2-octyne. Both groups obtained *cis*-9,*cis*-12-octadecadienoic acid as a yellowish liquid which on bromination gave tetrabromostearic acid identical with that obtained from natural linoleic acid.

Esterification is probably the most important reaction of linoleic acid. Monoesters are readily prepared by catalytic esterification, or by acid- or alkali-catalyzed alcoholysis of linoleic-rich oils. Linoleic acid forms salts, an acid chloride, amide, nitrile, etc., by the usual methods of preparing these derivatives.

Autoxidation of linoleic acid with atmospheric oxygen results in the formation of hydroperoxides with some shifting of the double bonds and formation of conjugated hydroperoxides (see Chapter XIV).

When methyl linoleate is heated to 200° C. with an excess of maleic anhydride, two moles of the latter add per mole of ester. The first mole of anhydride adds at one double bond thereby producing a conjugated sys-

tem, followed by the addition of a second mole by Diels-Alder reaction. The second mole adds by substitution giving an end product containing one double bond (401).

Linolelaidic Acid. *trans-9,trans-12*-Octadecadienoic (linolelaidic) is produced in small proportion when natural linoleic acid is treated with the oxides of nitrogen or by heating to 200° C. with selenium. Kass and Burr (402) obtained about 16% of linolelaidic acid (m.p. 28–29° C.) by isomerization of natural linoleic acid, which on bromination gave a crystalline tetrabromostearic acid melting at 78° C. and a liquid tetrabromostearic acid in about equal amounts. This linolelaidic acid also gave, after hydroxylation, two tetrahydroxystearic acids melting at 146° and 122° C., respectively.

These authors also reported the isolation of a liquid linolelaidic acid from the isomerization mixture which gave no solid tetrabromostearic acid but on hydroxylation yielded two tetrahydroxystearic acids melting at 156–158 and 126–127° C., respectively. It is probable that during the elaidinization some *cis-9,trans-12*- and *trans-9,cis-12*-octadecadienoic acids were produced.

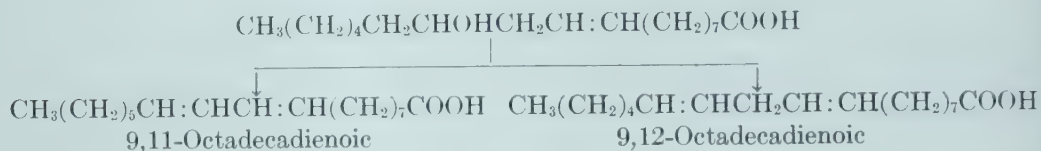
Alkali-Isomerized Octadecadienoic Acids. Natural linoleic (*cis,cis*) and linolelaidic (*trans-trans*) acids when heated to a high temperature (180° C.) with sodium hydroxide in a stable liquid (ethylene glycol) undergo shifts in their systems of double bonds, especially in the direction of conjugation. This shift is accompanied by geometric isomerization; consequently, the isomerization product consists of a mixture of positional and geometric isomers.

In 1951 Nichols *et al.* (403) reported that alkali-isomerization of linoleic and linolelaidic acids gave a mixture of *cis-9,trans-11*- and *trans-10,cis-12*-octadecadienoic acids melting at 22–23° and 3° C., respectively. The following year von Mikusch (404) reported that the mixture of alkali-isomerized linoleic acids also contains *cis-9,cis-11*- and *cis-10,cis-12*-octadecadienoic acids melting at 19–20° and 21–22° C., respectively. A year later, Ahlers *et al.* (405) assigned a *trans-9,trans-12* structure to an octadecadienoic acid melting at 42–43° C. which had been obtained by alkali-isomerization of linolelaidic acid.

As early as 1942 von Mikusch (406) reported the isolation, from the alkali-isomerized acids of dehydrated castor oil, a 10,12-linoleic acid melting at 57° C., apparently having a *trans,trans*-configuration.

Dehydrated Hydroxyoctadecenoic Acids. Ricinoleic acid, its monoesters, and glycerides (castor oil), when heated at 250° C. in the presence of a dehydrating agent, lose a molecule of water with the formation of

two positionally isomeric octadecadienoic acids as indicated in the following equation:



The number and diversity of products isolated from the mixture of dehydrated acids indicate that this reaction is also accompanied by both migration of the newly formed double bonds as well as simultaneous formation of geometric isomers.

A liquid acid was isolated from the reaction mixture and was presumed to be 9,12-octadecadienoic acid but it was not identical with natural linoleic acid (406). It probably comprised a mixture of *cis*-9,*trans*-12-, *cis*-9,*cis*-11-, and *cis*-9,*trans*-11-octadecadienoic acids.

As early as 1894 Mangold (407) reported the isolation from dehydrated ricinelaidic acid of a 9,11-linoleic acid melting at 43° C. which was shown in 1953 by Ahlers *et al.* (405) to be *trans*-9,*trans*-11 octadecadienoic acid.

In 1930 Smit and Böeseken (408) also reported the isolation from dehydrated elaidinized ricinoleic acid, a 9,11-linoleic acid melting at 54° C. to which they assigned a *trans,trans*-structure. Reinvestigation of Smit and Böeseken's acid by von Mikusch (409) led him to assign to it a structure corresponding to *trans*-8,*trans*-10-octadecadienoic.

Von Mikusch (410) isolated from dehydrated ricinelaidic acid a 10,12-linoleic acid melting at 57° C. which Ahlers *et al.* (405) as well as Witnauer *et al.* (411) have shown to be *trans*-10,*trans*-12-octadecadienoic.

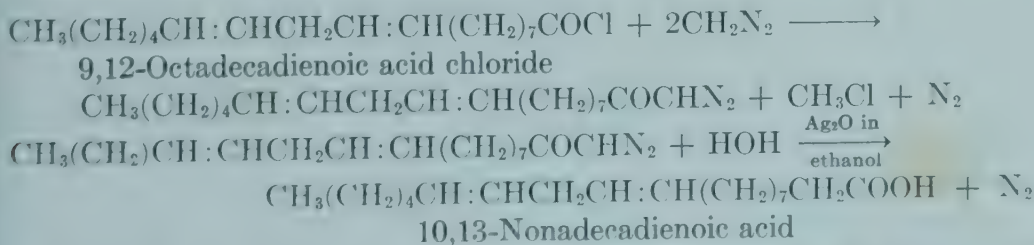
Octadecadienoic Acids Produced by Hydrogenation. Böeseken *et al.* (412) reported the formation of a 10,12-octadecadienoic acid melting at 29° C. as a product of partial hydrogenation of eleostearic (9,11,13-octadecatrienoic) acid. Lemon (413) reported the presence of an isomeric linoleic acid among the products of partial hydrogenation of linolenic (9,12,15-octadecatrienoic) acid. This isolinoleic acid was obtained as a concentrate but not as a pure product by fractional crystallization, distillation, and chromatographic adsorption of the acids derived from hydrogenated linseed oil.

Synthetic Octadecadienoic Acids. Schmid and Lehmann (414) described a method for preparing alkadienoic acids from monoalkenoic acids. They prepared *trans*-9,*trans*-11-octadecadienoic acid (m.p. 32–33° C.) by reacting the ester of elaidic acid with *N*-bromosuccinimide to give 11-bromocelaidic acid ester which when heated with collidine (2,4,6-trimethylpyridine) gave the desired acid.

Allen (414a) reported the synthesis of the methyl ester of the conjugated *cis*-10,*cis*-12-octadecadienoic acid. 10,12-Octadecadiynoic acid was prepared by oxidative coupling of 1-heptyne and 10-hendecynoic acid. The alkynoic acid was esterified with methanol and semihydrogenated in ethyl acetate in the presence of Lindlar catalyst. The reaction product was fractionally crystallized and methyl *cis*-10,*cis*-12-octadecadienoate was isolated. The ester melted at 1° C., had a refractive index n_D^{25} 1.4690, and was further characterized by its ultraviolet and infrared spectra, and by ozonolysis followed by identification of the dibasic cleavage products.

Other Natural Octadecadienoic Acids. There has been considerable speculation concerning the possible existence in natural fats of octadecadienoic acids other than linoleic. To date no such acid has been isolated, possibly owing to the limitation of the present techniques of separating closely related position isomers. There is some indirect evidence, however that positional or geometric isomers may be present in some fats, for example, codliver and whale oils (415), butterfat (416), milk fats (417) and the liver and depot fats of beef cattle and sheep (418). Until these suspected isomers are isolated and unequivocally characterized their existence will continue to be a subject of speculation.

Nonadecadienoic Acid, $C_{19}H_{34}O_2$. No nonadecadienoic acid has been found as a constituent of natural fats and only one isomer, namely, 10,13-nonadecadienoic acid, has been synthesized. Karrer and Koenig (419) prepared this isomer by applying the Arndt and Eistert chain-lengthening method (see Chapter XVIII) to linoleic acid. Linoleic acid was converted to the chloride and thence to the diazoketone by treatment of the chloride with diazomethane. The diazoketone was treated with silver oxide in ethanol and hydrolyzed to yield 10,13-nonadecadienoic acid. The reactions involved may be represented by the following equations:



Eicosadienoic Acids, $C_{20}H_{36}O_2$. Only one eicosadienoic acid appears to have been detected in natural fats. In 1942 Baudart (420) reported the presence of a small proportion of 11,14-eicosadienoic acid, $CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_9COOH$, in the total fatty acids of the liver oil of

a shark, *Carcharodon carcharis*. Later, the same author (421) reported the presence of an eicosadienoic acid in Cambodia fish oil. Karrer and Koenig (419) prepared 11,14-eicosadienoic acid by applying the Arndt-Eistert chain-lengthening reaction to 10,13-nonadecadienoic acid which was prepared in the same manner from linoleic acid as described above.

Docosadienoic Acids, $C_{22}H_{40}O_2$. Docosadienoic acids have been reported to be constituents of several oils of the Cruciferae family. Hilditch *et al.* (422) first reported the presence of a C_{22} -dienoic acid (2.3%) in a rapeseed oil (*Brassica campestris*) of East Indian origin. A year later Baliga and Hilditch (346) reported that the acid occurred to the extent of 0.5 to 1.5% of the total fatty acids of *Brassica* oils of various origins and that it was also present in Jamba rapeseed oil (*Eruca sativa*). Hatt and Szumer (273) reported the presence of 0.1% of a C_{22} -dienoic acid in the seed of Kerguelen cabbage (*Pringlea antiscorbutica*).

The C_{22} -dienoic acid found in these oils was not isolated in the pure state but Baliga and Hilditch (346) showed that it contained a pentadiene structure, $=CHCH_2CH=$, and that the unsaturation began at the 13th carbon atom. They also obtained 13,14,16,17-tetrabromodocosanoic acid melting at 106–107° C. on bromination of the impure acid.

Hexacosadienoic Acids, $C_{26}H_{48}O_2$. Bergmann and Swift (372) found that 17,20-hexacosadienoic acid, $CH_3(CH_2)_4CH:CHCH_2CH:CH-(CH_2)_{15}COOH$, comprised 40% of the total fatty acids of the lipids of the sponge, *Speciospongia vesparia*. The acid melted at 61° C. and gave a tetrabromohexacosanoic acid melting at 106–107° C.

(c) Alkatrienoic Acids, $C_nH_{2n-6}O_2$

The normal alkatrienoic (triethenoic, trienoic) acids are characterized by the presence of three double bonds in the hydrocarbon chain. With few exceptions these acids are found only in vegetable oils. Because of their relatively high degree of unsaturation they readily undergo oxidation and polymerization when exposed to air and elevated temperatures. When present in sufficient proportion these acids impart to oils the property of forming hard and durable films; hence such oils find employment in the protective and decorative coating industry.

The several double bonds of the triethenoic acids may occupy isolated or conjugated positions. The presence of conjugated bonds increases the rate of drying and imparts water- and alkali-resistance to the films. The double bonds of the triethenoic acids may not only occupy different positions in the carbon chain, but they may also occur in *cis* and *trans*-forms, thus multiplying the theoretically possible number of isomers.

Although the long-chain triethenoic acids are capable of existing in a considerable number of positionally and geometrically isomeric forms only a very few have been encountered in nature and these are confined to acids having 16 to 22 carbon atoms in the chain.

All of the triethenoic acids add six halogens or six hydroxyl groups to form hexahalogenated or hexahydroxylated acids, which derivatives are of primary importance in the identification and the determination of the structure of the individual acids.

The known naturally occurring alkatrienoic acids and artifacts produced from them are given in Table 17.

Hexadecatrienoic Acids, $C_{16}H_{26}O_2$. The hexadecatrienoic acids are the lowest molecular weight triethenoic acids which have been found to occur in natural fats; to date only two of these have been recognized, one from a marine animal source and the other from a vegetable lipid.

6,10,14-Hexadecatrienoic (hiragonic) acid, $CH_3CH:CH(CH_2)_2CH:CH(CH_2)_2CH:CH(CH_2)_4COOH$, was first reported in 1929 by Toyama and Tsuchiya (423) as a constituent of the body oil of the Japanese sardine, *Clupanodon melonostica*. The acid which is present in small proportion in this oil was shown by the authors to have the structure indicated above.

7,10,13-Hexadecatrienoic acid, $CH_3CH_2CH:CHCH_2CH:CHCH_2CH:CH(CH_2)_5COOH$, was isolated by Heyes and Shorland (424) in 1951 from the lipids of rape (*Brassica napus*) leaves. The acid comprised 11–17% of the total fatty acids of the leaf lipids. Oxidation of the acid with potassium permanganate gave pimelic, $CH_2(CH_2CH_2COOH)_2$, oxalic, and propionic acids which result, together with those obtained by spectrophotometric analysis of the acid before and after isomerization, led to the assignment of the structure indicated above.

Octadecatrienoic Acids, $C_{18}H_{30}O_2$. The largest number and best-known group of normal triethenoic acids contain 18 carbon atoms. The natural acids of this group include linoleic, eleostearic, puniceic, trichosanic, and several other lesser known isomers. Only one of these, namely, linolenic, is widely distributed in nature.

cis-9,*cis*-12,*cis*-15-Octadecatrienoic (linolenic) acid, $CH_3CH_2CH:CHCH_2CH:CHCH_2CH:CH(CH_2)_7COOH$, is of frequent occurrence in many seed fats, although often in very small proportion. The presence of linolenic acid in appreciable proportion markedly enhances the drying and film-forming properties of such oils. Oils containing relatively large proportions of linoleic acid, but less than 15% of linolenic acid, e.g., soybean, safflower, and walnut seed, find only limited use in the drying oil industry.

Systematic name	Common name	Formula, R—COOH
6,10,14-Hexadecatrienoic	Hiragonic	$\text{CH}_3\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_4-$
7,10,13-Hexadecatrienoic		$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_5-$
<i>cis</i> -6, <i>cis</i> -9, <i>cis</i> -12-Octadecatrienoic		$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_4-$
<i>cis</i> -9, <i>trans</i> -11, <i>trans</i> -13-Octadecatrienoic	α -Eleostearic	$\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})_3(\text{CH}_2)_7-$
<i>trans</i> -9, <i>trans</i> -11, <i>trans</i> -13-Octadecatrienoic	β -Eleostearic	$\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})_3(\text{CH}_2)_7-$
<i>cis</i> -9, <i>cis</i> -11, <i>trans</i> -13-Octadecatrienoic	Punicic ^a	$\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})_3(\text{CH}_2)_7-$
9,12,14-Octadecatrienoic		$\text{CH}_3(\text{CH}_2)_2(\text{CH}:\text{CH})_2\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_7-$
<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic	Linolenic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7-$
<i>trans</i> -9, <i>trans</i> -12, <i>trans</i> -15-Octadecatrienoic	Linolenelaidic ^b	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7-$
<i>trans</i> -10, <i>trans</i> -12, <i>trans</i> -14-Octadecatrienoic	Pseudoeleostearic	$\text{CH}_3(\text{CH}_2)_2(\text{CH}:\text{CH})_3(\text{CH}_2)_8-$
10,12,15-Octadecatrienoic		$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2(\text{CH}:\text{CH})_2(\text{CH}_2)_8-$
5,8,11-Eicosatrienoic		$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_5-$
8,11,14-Eicosatrienoic		$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_6-$
7,10,13-Docosatrienoic		$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_5-$
8,11,14-Docosatrienoic		$\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_6-$

^a Also trichosanic.^b Also elaidolinolenic.

principally in the manufacture of synthetic resins and in admixtures with more rapid drying oils in the manufacture of protective and decorative coating products, printing inks, linoleum, etc. When the proportion of linolenic acid exceeds 25% of the total fatty acids, the drying and film-forming properties of an oil become quite pronounced. Only a few oils of commerce, e.g., linseed, perilla, and hempseed, contain 25 to 50% of linolenic acid, together with an appreciable proportion of linoleic acid. It is these oils, therefore, that find direct employment in the manufacture of house paints and related products.

Linolenic acid was first recognized by Hazura and Friedreich (425) in 1887 as a constituent of hempseed (*Cannabis sativa*) oil. These authors also demonstrated that the acid contained three double bonds since it formed a hexahydroxystearic acid on oxidation and a hexabromostearic acid on bromination. Erdmann, Bedford, and Raspe (426) on the basis of ozonolysis studies established the positions of the double bonds as indicated above. This structure was subsequently verified by other investigators (427).

8, $C_{18}H_{32}O_2$

Formula weight	M p., ° C.	B p., ° C/mm.	Theoret. iodine value	Neutral- ization value	Source
250.37			304.16	224.08	Sardine oil
250.37			304.16	224.08	<i>Brassica napus</i> leaves
278.42			273.51	201.51	Evening primrose oil
278.42	48-49	235/12	273.51	201.51	Tung, po-yak, neou, etc.
278.42	71.5		273.51	201.51	Isomerization eleostearic
278.42	43.5		273.51	201.51	Pomegranate, snake gourd
278.42			273.51	201.51	Alkali isomerization linolenic
278.42	-10 to -11.3	157/0.001	273.51	201.51	Linseed, perilla, hemp, etc.
278.42	29-30		273.51	201.51	Elaidinization linolenic
278.42	79		273.51	201.51	Alkali isomerization linolenic
278.42			273.51	201.51	Alkali isomerization linolenic
306.47			248.48	183.06	Brain phosphatides
306.47			248.48	183.06	Shark liver oil
334.52			227.64	167.71	Brain phosphatides
334.52			227.64	167.71	Shark liver oil

Although the chain length and the positions of the double bonds were firmly established, the geometric configurations were not clarified until much later. Because linolenic acid gave a solid (m.p. 181° C.) and a liquid hexabromostearic acid on bromination and two hexahydroxystearic acids (linusic, m.p. 203° C.; isolinusic, m.p. 174° C.) on oxidation with alkaline potassium permanganate, it was presumed by some investigators that natural linolenic acid consisted of a mixture of two geometric isomers, although others held that the acid was homogeneous, but underwent isomerization at the instant bromination and hydroxylation occurred. This question was definitely resolved by the application of infrared spectroscopy by McCutcheon *et al.* (394) and Ahlers *et al.* (394) which revealed evidence that linolenic acid possessed a *cis,cis,cis*-configuration. Linolenic acid is the only isomer of the eight possible geometric isomers of 9,12,15-octadecatrienoic acid which has been found in nature.

When pure, linolenic acid is a colorless liquid which can be distilled at $157-158^{\circ}$ C. under a pressure of 0.001 mm. In the solid state it melts at -11.0° to -11.3° C. The acid (or its esters) readily autoxidizes and

forms hard films when exposed to atmospheric oxygen. On heating to elevated temperatures it undergoes thermal polymerization. At a temperature of 200° C. it reacts with three moles of maleic anhydride, the first two of which react to saturate two double bonds, probably by inducing conjugation, followed by a Diels-Alder reaction. The third mole adds by substitution without saturating the remaining double bond (401).

Treatment of linolenic acid in the form of its ethyl ester with 1% selenium at 205–215° C. under nitrogen converts it to linolenelaidic (elaidolinolenic) acid melting at 29–30° C. (427a), which has been shown by infrared spectral analysis to be *trans*-9,*trans*-12,*trans*-15-octadecatrienoic acid (405). Linolenelaidic acid forms a solid hexabromostearic acid melting at 169–170° C., and an ethyl ester melting at 114–115° C.

cis-6,*cis*-9,*cis*-12-Octadecatrienoic acid is the only position isomer comparable to linolenic acid which has been observed in a natural fat. The presence of this acid in the seed oil of the evening primrose (*Oenothera biennis*) was first suggested by Heiduschka and Lüft (428) and it was subsequently investigated by Eibner *et al.* (429) and Riley (430). The same acid was later reported by Tsuchiya (431) to be present in another species of the same genus, *O. Lamarckiana*.

6,9,12-Octadecatrienoic acid comprises about 10% of the total fatty acids of the seed oil of the evening primrose. Its structure was established by ozonolysis (430) and by isomerization with alkali at 180° C. On bromination it yields a hexabromostearic acid melting at 196° C. and on oxidation with alkaline potassium permanganate, a hexahydroxystearic acid melting at 245° C.

cis-9,*trans*-11-*trans*-13-Octadecatrienoic (eleostearic) acid, $\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})_2(\text{CH}_2)_7\text{COOH}$, appears to have been noted first by Clöez (432) in 1887 as a constituent of Japanese tung (*Aleurites cordata*) oil. He assigned to it the formula $\text{C}_{17}\text{H}_{30}\text{O}_2$ which was accepted until 1902 when Maquenne (433) proposed for it the formula $\text{C}_{18}\text{H}_{30}\text{O}_2$, and also suggested the designation α -eleostearic and β -eleostearic for the low and high-melting forms of the acid. Both forms of the acid absorb bromine to form a tetrabromide melting at 115° C. For many years these acids were assumed to have only two double bonds, hence various branched-chain structures were assigned to them to correspond with the molecular formula. As early as 1913 Fokin (433a) suggested that the double bonds in eleostearic acid were conjugated and in 1919 Majima (434) found that hydrolysis of eleostearic acid ozonide yielded *n*-valeric aldehyde, $\text{CH}_3(\text{CH}_2)_3\text{CHO}$, *n*-valeric acid, $\text{CH}_3(\text{CH}_2)_3\text{COOH}$, and aze-laic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOH}$. Both investigators, however, still assumed the presence of only two double bonds in the carbon chain.

It was not until 1925 that Böeseken and Ravenswaay (435) concluded on the basis of the high molecular refractivity of the acid and the fact that it absorbed three moles of hydrogen that its structure corresponded to $\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_3)_7\text{COOH}$. Eibner and Rossmann (436) confirmed this structure when they obtained a yield of 60% of glyoxal ($\text{OHC}-\text{CHO}$) on hydrolysis of the eleostearic acid ozonide and no succinic acid $(\text{CH}_2\text{COOH})_2$. Further confirmation was obtained by Bauer and Rohrbach (437) who obtained a hexabromostearic acid (m.p. $139-141^\circ \text{C}$.) by complete bromination of α -eleostearic acid, and by van Loon (438) who obtained a hexabromostearic acid (m.p. 157°C .) on complete bromination of β -eleostearic acid and further bromination of the tetrabromide melting at 114.8°C .

By 1930 the correct structural formula for eleostearic acid had been established but not its geometric configuration. Morrell and co-workers (439), Rinkes (440), and others carried out many investigations on the maleic anhydride addition products of α - and β -eleostearic acids without arriving at the correct geometric configurations of the two acids. These were finally settled in 1953 by the application of infrared absorption measurements to the maleic anhydride adducts by Paschke, Tolberg, and Wheeler (441) and to the acids by Ahlers *et al.* (405) and by Bickford *et al.* (442). These investigators assigned to α -eleostearic acid a *cis*-9, *trans*-11, *trans*-13 configuration, and to β -eleostearic acid a *trans*-9, *trans*-11, *trans*-13 configuration. These two forms of 9,11,13-octadecatrienoic acid represent two of the eight possible geometrical isomers of this acid.

Carefully isolated eleostearic acid from fresh tung oil melts at $48-49^\circ \text{C}$., but it is readily transformed by the action of light or by contact with iodine or sulfur into a white solid melting at 71°C . Eleostearic acid contains the same number of double bonds as linolenic acid, but they are arranged in alternate (or conjugated) positions instead of isolated or methylene-interrupted positions. Compared to the methylene-interrupted arrangements of bonds in linolenic acid, the conjugated system produces such effects as exalted molecular refractivity, shifts in the infrared absorption spectra, increased rates of oxygen absorption and film formation, increased water- and alkali-resistance to air-dried films, gelation on heating, and decreased absorption of halogens from Wijs and Hanus solutions. α -Eleostearic acid and its β -isomer react with maleic anhydride to yield Diels-Alder adducts melting at 62.5° and 77°C ., respectively. Both acids yield tetra- and hexabromides depending on the conditions of halogenation.

Complete catalytic hydrogenation of either isomer yields stearic acid. When α -eleostearic acid esters are hydrogenated, with or without solvent, the reaction proceeds by stepwise addition to form first a mixture in equimolar proportions of 9-, 10-, 11-, 12-, and 13-octadecenoates (443). Apparently no stearate is formed until all the eleostearate is converted to octadecenoates.

In Table 18 there are listed the principal plant sources from which eleostearic acid has been isolated or detected, together with the weight-per cent of the acid in the mixed fatty acids in which it has been found.

cis-9,*cis*-11,*trans*-13-Octadecatatrienoic (punicic) acid was first isolated in 1935 by Toyama and Tsuchiya (444) from pomegranate (*Punica granatum*) seed oil in which it comprises 72% of the total fatty acids. The acid, which melts at 44° C. and is isomeric with eleostearic acid, was named puniceic acid. The isomeric structure was confirmed by Farmer and van den Heuvel (445) and in 1954 Ahlers *et al.* (446) reported that it possessed a *cis,cis,trans*-configuration (probably *cis*-9,*cis*-11,*trans*-13). The acid does not form an adduct with maleic anhydride according to Paschke *et al.* (441). Under the influence of light puniceic acid is converted to β -eleostearic acid.

In the same communication in which Toyama and Tsuchiya (444) reported the isolation of puniceic acid they described the isolation of another acid from the seed fat of the Japanese snake gourd (*Trichosanthes cucumeroides*). This acid which comprised 30% of the total fatty acids melted at 35.0–35.5° C. and, like puniceic acid, it was converted into β -eleostearic acid under the action of light. The acid was named trichosanic and was assumed to be a fourth geometrical isomer of eleostearic acid.

Kaufmann *et al.* (447) reported the presence of 29.3% of this acid in a sample of the seed oil of the same species and later Ahlers and Dennison (448) reported, on the basis of ultraviolet absorption measurements, that the oil contained 37% of this acid.

Soni and Aggarwal (449) found the seed oil of the Indian snake gourd (*T. Anguina*) contained 42.3% of trichosanic acid and later, on the basis of ultraviolet absorption measurements, Ahlers and Dennison (448) reported its presence in the same oil to the extent of 41%.

On the basis of the similarity of the ultraviolet and infrared absorption spectra of pomegranate and the two snake gourd oils Ahlers *et al.* (446) concluded that puniceic and trichosanic acids were identical despite the marked differences in the melting points of the two acids. The fact that the three oils show the same absorption characteristics does not entirely

TABLE 18
Oils Containing Eleostearic Acid

Scientific name	Common name	Per cent	Author-ity
<i>Aleurites cordata</i>	Japanese tung	74	^a
<i>Aleurites fordii</i>	Chinese wood	77-86	^b
<i>Aleurites montana</i>	Mu, abrasin	71-82	^c
<i>Aleurites trisperma</i>	Banucalag, baguilumbang	51-67	^d
<i>Garcia nutans</i>	Pinonchillo	93-95	^e
<i>Licania rigida</i>	Oiticica	16-17	^f
<i>Mallotus philippinensis</i>	Kamala	38	^g
<i>Parinarium campestre</i>	Fungu, behurada	49	^h
<i>Parinarium corymbosum</i>	Taritih	13-15	ⁱ
<i>Parinarium laurinum</i>	Makita	30-34	^j
<i>Parinarium macrophyllum</i>	Neou	30-32	^k
<i>Parinarium sherbroense</i>	Po-yak	32-37	^l
<i>Ricinodendron africanum</i>	Essang	49-53	^m
<i>Telfairia occidentalis</i>	Krobanko	19	ⁿ

^a R. S. McKinney and G. S. Jamieson, *Oil & Soap*, **14**, 2-3 (1937).

^b R. L. Holmes, F. C. Pack, J. C. Minor, and R. S. McKinney, *J. Am. Oil Chemists' Soc.*, **31**, 417-418 (1954); R. T. O'Connor, D. C. Heinzelman, R. S. McKinney, and F. C. Pack, *ibid.*, **24**, 212-216 (1947); T. P. Hilditch and J. P. Riley, *J. Soc. Chem. Ind. London*, **65**, 74-81 (1946).

^c R. W. Planck, F. C. Pack, and D. B. Skau, *Abstract Bibliography of the Chemistry and Technology of Tung Products, 1875-1950*. U. S. Dept. Agr., Bur. Agr. Ind. Chem., AIC-317. New Orleans.

^d R. S. McKinney and G. S. Jamieson, *Oil & Soap*, **12**, 146-148 (1935); E. D. G. Frahm and D. R. Koolhaas, *Rec. trav. chim.*, **58**, 277-282 (1939).

^e G. S. Jamieson and W. G. Rose, *Oil & Soap*, **20**, 202-203 (1943).

^f A. Mendelowitz, Thesis, University of Liverpool, 1952, pp. 150-160.

^g S. V. Puntambekar, *Proc. Indian Acad. Sci.*, **35A**, 57-68 (1952).

^h A. Steger and J. van Loon, *Fette u. Seifen*, **49**, 769-770 (1942).

ⁱ E. D. G. Frahm, *Ing. Ned. Indië*, **8**, No. 9, VII, 92-98 (1942).

^j G. Winter, *Paint Notes*, Dept. Munitions, Australia, **3**, No. 12, 393-406 (1948); J. P. Riley, *J. Chem. Soc.*, **1950**, 12-18.

^k A. Steger and J. van Loon, *Rec. trav. chim.*, **53**, 197-204 (1934); N. Ivanov, *Bull. soc. chim. France* [5] **11**, 404-406 (1944); T. P. Hilditch and J. P. Riley, *J. Soc. Chem. Ind. London*, **65**, 74-81 (1946).

^l A. Steger and J. van Loon, *Rec. trav. chim.*, **57**, 620-628 (1938).

^m A. Steger and J. van Loon, *Rec. trav. chim.*, **54**, 988-994 (1935).

ⁿ T. P. Hilditch and J. P. Riley, *J. Soc. Chem. Ind. London*, **65**, 74-81 (1946).

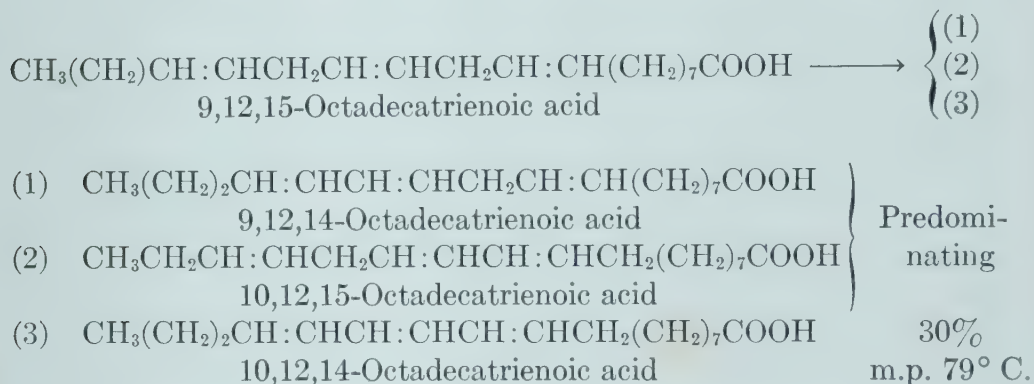
rule out the possibility that one acid may have a *cis,cis,trans*- and the other a *trans,cis,cis*-configuration.

Other Octadecatrienoic Acids. In addition to the natural octadecatrienoic acids described above several others have been prepared artificially.

These isomers have been prepared by the action of caustic alkali on linolenic acid or its esters at high temperature in the presence of organic solvents, or at low temperature by the action of sodium amide in the presence of liquid ammonia.

Moore (450) was the first to note (1937) that prolonged treatment of linseed oil with an excess of potassium hydroxide in ethanol solution resulted in the partial conversion of the 9,12,15-linolenic ester to a product exhibiting strong absorption maxima at 2300 and 2700 Å., characteristic of the presence of conjugated double bonds. He found that the absorption was produced by an acid melting at 77° C. which appeared to be an isomer of eleostearic acid.

It was subsequently concluded that alkali isomerization of linolenic acid produced predominantly a mixture of fatty acids containing conjugated diene systems and an isolated double bond, together with about 30% of a conjugated trienoic acid as shown schematically below:



In 1939 Kass *et al.* (451) published the results of an extensive investigation of the action of excess potassium hydroxide on the fatty acids of linseed oil dissolved in boiling butanol and anhydrous ethylene glycol. From the reaction products they isolated a conjugated fatty acid which melted at 79° C. The acid gave a methyl ester melting at 41° C. and a tetrabromide melting at 104.5° C. On bromination in the presence of ultraviolet light it gave a hexabromostearic acid melting at 152.5° C. On oxidation there was obtained sebacic, oxalic, and *n*-butyric acids indicating a structure corresponding to 10,12,14-octadecatrienoic acid.

In 1955 Abu-Nasr and Holman (452) reported the results of an investigation of the action of sodium amide on methyl linolenate in liquid ammonia at a temperature of -32° C. in which the only variable was time. They found that the reaction product consisted of a mixture of amides and esters of *cis,trans*-diene-conjugated triene; all *trans*- and possibly *cis, cis*,

trans- or all *cis*-conjugated triene; and conjugated triene of the punicic acid type.

Eicosatrienoic Acids, $C_{20}H_{34}O_2$. Two eicosatrienoic acids, namely, 5,8,11- and 8,11,14-eicosatrienoic, have been reported from natural sources. Klenk *et al.* (453) reported the presence of 5,8,11-eicosatrienoic acid in brain phosphatides together with other C_{20} -acids of lower and higher unsaturation, 11-eicosenoic, 11,14-eicosadienoic, and 5,8,11,14-eicosatetraenoic.

Baudart (454) found a small proportion of 8,11,14-eicosatrienoic acid in the liver oil of the shark *Carchardodon carcharias*, together with the related 11,14-eicosadienoic acid. Shortly thereafter he reported that the same two acids were present in Cambodia fish oil.

Docosatrienoic Acids, $C_{22}H_{38}O_2$. Two docosatrienoic acids, namely, 7,10,13- and 8,11,14-docosatrienoic, have been reported from natural sources. Klenk *et al.* (453) reported the presence of 7,10,13-docosatrienoic acid as a constituent of brain phosphatides, together with five other more highly unsaturated acids of the same carbon chain length.

Baudart (454) found 8,11,14-docosatrienoic acid, together with a less highly and a more highly unsaturated C_{22} -acid to be constituents of the liver oil of the shark *Carcharodon carcharias*.

(d) *Alkatetraenoic Acids, $C_nH_{2n-8}O_2$*

With one exception the known alkatetraenoic (tetraethenoic, tetraenoic) acids are found only in animal fats and principally in marine animal oils. The ready oxidation of fish oils is due to the presence of these and more highly unsaturated acids containing 16 to 26 carbon atoms, but principally to those with 20 and 22 carbon atoms.

Data with reference to the molecular properties of the alkatetraenoic and more highly unsaturated alkenoic acids are given in Table 19.

Hexadecatetraenoic Acids, $C_{16}H_{24}O_2$. The first hexadecatetraenoic acid isolated from a natural source was the 4,8,11,14-isomer which was found by Tutiya (455) to be present in the body oil of the sardine. Later the 6,9,12,15-isomer was reported by Silk and Hahn (456) to be present in the fatty acids derived from South African pilehard oil.

Octadecatetraenoic Acids, $C_{18}H_{28}O_2$. At least two octadecatetraenoic acids have been found in nature, one in a seed fat and the other in marine animal oils.

4,8,12,15-Octadecatetraenoic (moroctic, stearidonic) acid was the first of the two octadecatetraenoic acids to be recognized. As early as 1906

TABLE
Alkatetraenoic Alkapentaenoic,

Systematic name	Common name	Molecular formula	Structural formula, R—COOH
4,8,11,14-Hexadecatetraenoic		C ₁₆ H ₂₄ O ₂	CH ₃ (CH:CHCH ₂) ₃ CH ₂ CH:CH(CH ₂) ₂ —
6,9,12,15-Hexadecatetraenoic		C ₁₆ H ₁₄ O ₂	CH ₂ :CHCH ₂ (CH:CHCH ₂) ₃ (CH ₂) ₃ —
4,8,12,15-Octadecatetraenoic	Moroctic ^a	C ₁₈ H ₂₈ O ₂	CH ₃ CH ₂ (CH:CHCH ₂) ₂ (CH ₂ CH:CHCH ₂) ₂ CH ₂ —
9,11,13,15-Octadecatetraenoic	α-Parinaric	C ₁₈ H ₂₈ O ₂	CH ₃ CH ₂ (CH:CH) ₄ (CH ₂) ₇ —
9,11,13,15-Octadecatetraenoic	β-Parinaric	C ₁₈ H ₂₈ O ₂	CH ₃ CH ₂ (CH:CH) ₄ (CH ₂) ₇ —
4,8,12,16-Eicosatetraenoic		C ₂₀ H ₃₂ O ₂	CH ₃ CH ₂ (CH ₂ CH:CHCH ₂) ₄ CH ₂ —
5,8,11,14-Eicosatetraenoic	Arachidonic	C ₂₀ H ₃₂ O ₂	CH ₃ (CH ₂) ₄ (CH:CHCH ₂) ₄ (CH ₂) ₂ —
6,10,14,18-Eicosatetraenoic		C ₂₀ H ₃₂ O ₂	CH ₃ CH:CHCH ₂ (CH ₂ CH:CHCH ₂) ₃ (CH ₂) ₃ —
4,7,10,13-Docosatetraenoic		C ₂₂ H ₃₆ O ₂	CH ₃ (CH ₂) ₇ (CH:CHCH ₂) ₄ CH ₂ —
7,10,13,16-Docosatetraenoic		C ₂₂ H ₃₆ O ₂	CH ₃ (CH ₂) ₄ (CH:CHCH ₂) ₄ (CH ₂) ₄ —
8,12,16,19-Docosatetraenoic ^b		C ₂₂ H ₃₆ O ₂	CH ₃ CH ₂ CH:CH(CH ₂ CH:CHCH ₂) ₃ (CH ₂) ₅ —
4,8,12,15,18-Eicosapentenoic	Timnodonic	C ₂₀ H ₃₀ O ₂	CH ₃ (CH:CHCH ₂) ₃ (CH ₂ CH:CHCH ₂) ₂ CH ₂ —
4,7,10,13,16-Docosapentenoic		C ₂₂ H ₃₄ O ₂	CH ₃ (CH ₂) ₄ (CH:CHCH ₂) ₅ CH ₂ —
4,8,12,15,19-Docosapentenoic ^c	Clupanodonic	C ₂₂ H ₃₄ O ₂	CH ₃ (CH ₂ CH:CHCH ₂) ₂ CH:CHCH ₂ (CH ₂ CH:CHCH ₂) ₂ CH ₂ —
Tetracosapentenoic	Scoliodonic	C ₂₄ H ₃₈ O ₂	Structure unknown
Hexacosapentenoic	Shibic	C ₂₆ H ₄₂ O ₂	Structure unknown
4,7,10,13,16,19-Docosahexaenoic		C ₂₂ H ₃₂ O ₂	CH ₃ CH ₂ (CH:CHCH ₂) ₆ CH ₂ —
4,8,12,15,18,21-Tetracosahexaenoic	Nisinic	C ₂₄ H ₃₆ O ₂	CH ₃ CH ₂ (CH:CHCH ₂) ₄ (CH ₂ CH:CHCH ₂) ₂ CH ₂ —
Hexacosahexaenoic	Thynnic	C ₂₆ H ₄₀ O ₂	Structure unknown

^a Also stearidonic.^b One of the two structures assigned this acid.^c One of the five structures assigned this acid.

Tsujimoto (457) suggested that the acid was present in fish oils; this suggestion was confirmed by Brown and Beal (458) in 1923 and by Suzuki and Masuda (459) in 1928. The acid was first thoroughly investigated by Toyama and Tsuchiya (460) who isolated it from Japanese sardine oil via the octabromide. Complete hydrogenation gave stearic acid and ozonolysis of the methyl ester and the tetracyanate indicated that the structure corresponded to 4,8,12,15-octadecatetraenoic acid. It has also been reported to be a minor constituent of the head oil of the white whale. An octadecatetraenoic acid has been reported (270a) to be present in the body fat of the mink to the extent of 2.3%.

9,11,13,15-Octadecatetraenoic (parinaric) acid was first isolated by Tsujimoto and Koyanagi (461) in 1933 from makite (*Parinarium laurinum*) seed fat in which it comprises 46–56% of the total fatty acids. Tutiya (462) found the acid to be present in balsam (*Impatiens balsamina*) seed fat. Kaufmann and Keller (463) found the acid to be a constituent of the seed fats of other species of this genus, namely, *I. fulva*, 51%; *I. parviflora*, 46%; *I. Roylei*, 40–50%; *I. nolimetangre*, 32%; *I.*

Alkahaenoic Acids

Formula weight	Melting point, ° C.	Neutralization value	Theoret. iodine value	Source
248.35		225.90	408.84	Sardine oil
248.35		225.90	408.84	Pilchard oil
276.40		202.98	367.34	Sardine oil, head oil of white whale
276.40	85-86	202.98	367.34	Seed oils of <i>Parinarium</i> and <i>Impatiens</i>
276.40	95-96	202.98	367.34	Isomerization of α -acid
304.46		184.28	333.50	Sardine and fish oils generally, whale and pig liver
304.46	-49.5	184.28	333.50	Brain, liver, glandular organs, egg, etc.
304.46		184.28	333.50	Fish oils generally
332.51		168.73	305.36	Brain phosphatides
332.51		168.73	305.36	Brain phosphatides
332.51		168.73	305.36	Shark liver oil
302.44		185.50	419.65	Sardine and bonito oils
330.49		169.76	384.03	Brain phosphatides
330.49	-78	169.76	384.03	Sardine, sturgeon, white fish, pilchard, codliver, and other fish oils
358.54		156.48	353.98	Shark liver oil
386.60		144.86	328.30	Tuna liver oil
328.48		170.80	463.67	Brain lipides
356.53		157.36	427.18	Japanese sardine oil
384.58		145.88	396.02	Bluefin tuna liver oil

hortensis, 27%; *I. sultanii*, 27%; and *I. Holstii*, 13%. Kaufmann (463) also reported the acid to be present in certain aquatic plants including a species of *Iris* and *Nymphaea alba*.

Farmer and Sunderland (464) established the fact that the structure of parinaric acid corresponded to the formula $\text{CH}_3\text{CH}_2(\text{CH}:\text{CH})_4(\text{CH}_2)_7\text{COOH}$. The acid is therefore unique among the vegetable oil fatty acids because it has four double bonds and also because all four of the bonds are conjugated. Ahlers *et al.* (405) concluded from the infrared absorption spectra of the acid that it contained either two *cis*- and two *trans*-, or one *cis*- and three *trans*-ethenoic groups.

Tsujimoto (465) observed that parinaric acid (m.p. 85-86° C.), when exposed to light or an isomerizing catalyst was converted to another form melting at 95-96° C., and therefore designated the two forms as α -parinaric and β -parinaric in analogy to α -eleostearic and β -eleostearic acids.

Eicosatetraenoic Acids, $\text{C}_{20}\text{H}_{32}\text{O}_2$. Several eicosatetraenoic acids have been isolated from marine animal oils. Two isomeric eicosatetraenoic acids, namely the 4,8,12,16- and the 6,10,14,18-isomers, have been isolated

from fish oils and identified. Both are said to be of general occurrence in these oils. Another isomer, namely, 5,8,11,14-eicosatetraenoic (arachidonic), is confined to the fats of land animals.

4,8,12,16-Eicosatetraenoic acid was first isolated by Toyama and Tsuchiya (466) from sardine oil and since then it has been reported to be present in other fish as well as whale oils. The structure of the acid was established by hydrogenation to arachidic acid and by ozonolysis of the amyl ester. Shimooka and Toyama (466a) reported the isolation of the same acid from the lipids of pig liver.

5,8,11,14-Eicosatetraenoic (arachidonic) acid was first isolated in 1909 by Hartley (467) who obtained it from liver lipids in the form of the octobromide. Since then arachidonic acid has been found as a constituent of the lipids from various organs of many terrestrial animals.

Levene *et al.* (468) reported the presence of arachidonic acid in liver, egg and brain lecithins, and brain cephalin. Wesson (469) found the acid in brain cephalin, the tissue and liver lipids of the rat, in liver, pancreas, kidney, lung, spleen, and lymph gland lipids, and in the muscle fat of the dog. It has been found to comprise 2.1% of the fatty acids of pork fat (470) and has been detected in the depot fat of the pig and ox (471), duck, goose, and chicken (472), and human fat (473).

Kimura (474) found arachidonic acid in the liver lipids of the ox and Suzuki (475) reported it to be present in small proportion in the lipids of Chinese egg yolk. Snider and Bloor (476) found arachidonic acid in liver lecithin and Bloor (477) isolated it from the lipids of beef heart. Bosworth and Sisson (478) reported it to be present in butter fat. According to Levene and Rolf (468) and Wesson (469), arachidonic acid occurs in both the lecithin and cephalin fractions of the brain. Brown (479) reported that arachidonic acid comprised 0.4% of the fatty acids of the lipids of the thyroid, 4.0% of the spleen, and 5.5% of the suprarenals. Subsequent work by Brown and co-workers (480) indicated that arachidonic acid comprised 11.2% of the total fatty acids of the suprarenal glands and 22% of the suprarenal phosphatides. According to Ault and Brown (480) suprarenal phosphatides are the best practical source for isolating this acid, but according to Holman (481) bull testicle tissue is even better. Brown (482) concluded that arachidonic is the only highly unsaturated acid present in the liver in which it comprises 2.0–7.7% of the total fatty acids of the lipids. Longenecker (483) found that arachidonic acid comprised 2.2% of the total fatty acids of the rat. It was found by Cartland and Hart (484) to be a constituent of the corpus luteum. Karkhanis and Magar (484a) reported the presence of arachidonic acid

in the body fat of two Indian marine fishes (black pomfret, 6.74%; pala, 0.48%) and in the fat of an Indian snake (*Python stinotis*, 0.8%).

On bromination, arachidonic acid yields a white crystalline octobromide which darkens but does not melt at 230–250° C. The bromide is insoluble in cold diethyl ether and only very slightly soluble in hot benzene and butanol. Several esters of the octobromide have been prepared by Shinowara and Brown (485) who reported the following melting points for them: methyl, 227–230°; ethyl, 226–227°; *n*-propyl, 223–224°; *n*-butyl, 222–223°; and *n*-amyl, 221.5–222.5° C.

On complete hydrogenation arachidonic acids yields arachidic acid and on oxidation with dilute potassium permanganate solution it yields a white crystalline octahydroxyarachidic acid (m.p. 195° C.) which is soluble in hot water. Ozonolysis of the acid yields a tetraozonide which upon cautious decomposition with aqueous hydrogen peroxide gives a mixture of mono- and dicarboxylic acids indicative of a structure (486) corresponding to $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:-\text{CH}(\text{CH}_2)_3\text{COOH}$.

Because of its tendency to undergo oxidation it is difficult to prepare and handle pure arachidonic acid; consequently most of the recorded properties refer to the methyl ester admittedly containing several per cent of impurity. The best values for the ester appear to be as follows: m.p., < –78° C.; b.p. at 1 mm., 160–165° C.; n_D^{20} , 1.4825; d_4^{20} , 0.9082.

Arachidonic acid, together with linoleic and linolenic acids, is classed as an essential fatty acid. Since arachidonic acid is not ordinarily a component of ingested foods its origin is difficult to explain. However, some authors believe that the acid is actually formed in the animal liver from ingested linoleic and linolenic acids.

Docosatetraenoic Acids, $\text{C}_{22}\text{H}_{36}\text{O}_2$. Three docosatetraenoic acids have been reported to be constituents of natural fats, two of which are present in brain phosphatides and a third in shark liver oil.

4,7,10,13-Docosatetraenoic acid was reported by Klenk and Bongard (453) to be present in the phosphatides of brain tissue, together with other highly unsaturated C_{22} -acids ranging from trienoic to hexaenoic.

7,10,13,16-Docosatetraenoic acid was also reported by Klenk and Bongard (453) to be a constituent of brain phosphatides.

8,12,16,19 (or 20)-Docosatetraenoic acid was the first C_{22} -tetraenoic acid found in nature. Baudart (454) reported its presence in small proportion among the fatty acids isolated from the liver oil of the shark, *Carcharodon carcharias*.

(e) *Alkapentaenoic Acids*, $C_nH_{2n-10}O_2$

The known alkapentaenoic (pentaethenoic, pentaenoic) acids derived from natural sources are confined to the normal series and with few exceptions they are constituents of animal fats. The acids recognized to date contain 20 to 26 carbons in the skeleton.

Eicosapentaenoic Acids, $C_{20}H_{30}O_2$. Toyama and Tsuchiya (487) reported the isolation of an eicosapentaenoic acid from sardine oil which they named timnodonic acid. They established the structure of the acid by ozonolysis of the amyl ester to be 4,8,12,15,18-eicosapentaenoic. The same acid was reported by Matsuda (488) to occur in bonito fish oil.

Herb *et al.* (488a) isolated an eicosapentaenoic acid, as well as a docosapentaenoic acid, from the highly unsaturated fraction of beef adrenal lipids but did not determine the structure of either acid.

Docosapentaenoic Acids, $C_{22}H_{34}O_2$. The best known docosapentaenoic acid is clupanodonic, which was isolated from Japanese sardine oil by Tsujimoto (489) in 1906. When first isolated it was thought to be a C_{18} -acid, but in 1920 Tsujimoto (489) concluded that it corresponded to the formula $C_{22}H_{34}O_2$. Still later, Tsujimoto (490) separated the fatty acids of sardine oil by the lithium salt-acetone and polybromide methods followed by repeated fractional distillation of the separated products. In this manner he obtained a nearly pure clupanodonic acid which he described as a light yellow liquid which became semisolid at -78°C . The density of the acid was reported to be 0.9385₄¹⁵ and the refractive index as 1.53039_D¹⁵.

Toyama and Tsuchiya (491) concluded on the basis of their studies of the products of ozonolysis of the amyl ester and the di- and tetrabromides of clupanodonic acid, and subsequently, of the potassium permanganate oxidation of methyl and potassium clupanodonate in acetone and aqueous solutions, that the acid was either 4,7,11,15,19- or more probably 4,8,12,15,19-docosapentaenoic, rather than 4,8,11,15,19-docosapentaenoic suggested by Tsujimoto (490) in 1928.

The structure of clupanodonic acid was a matter of controversy for years and on the basis of the review of the subject by Lovern (491a) in 1942 it was still unsettled at that time. The isolation from sardine and bonito oils and from codliver oil of a docosahexaenoic acid, $C_{22}H_{32}O_2$, which may or may not be identical with the clupanodonic acid investigated by Toyama and Tsuchiya (491) has not aided in clarifying the subject (see docosahexaenoic acid).

Clupanodonic acid has been detected in the body oils of a large number

of teleost fish in which it comprises 10 to 22% of the total fatty acids; also in the liver oils of this group of fishes, in which it comprises 12 to 14% of the total acids. It has been detected in various liver oils of marine elasmobranch fish in which it comprises 14 to 30% of the total fatty acids. It has also been found to comprise 2 to 9% of the total fatty acids of the body fats of various fresh water fish; 10 to 18% of the total fatty acids of seal blubber fats; and 13 to 15% of whale milk fats.

An unusual occurrence of clupanodonic acid was reported by Sueyoshi and Furukubo (492) who isolated it from Japanese egg lecithin. In view of the observations of Sinclair (493) that the composition of animal lecithins may vary with the nature of the ingested diet, Deuel (494) suggested that the presence of clupanodonic acid in Japanese egg lecithin may have been due to the presence of fish oil (meal) in the diet of the hen.

Klenk and Bongard (453) separated from brain phosphatides a series of C_{22} -acids including one which was identified as 4,7,10,13,16-docosapentaenoic.

Herb *et al.* (488a) isolated, but did not identify structurally, a docosapentaenoic acid from beef adrenal lipids.

Tetracosapentaenoic Acids, $C_{24}H_{38}O_2$. The only tetracosapentaenoic acid recognized to date is scoliiodonic, which has been detected as a minor component of shark-liver oils. Its structure is unknown.

Hexacosapentaenoic Acids, $C_{26}H_{42}O_2$. A hexacosapentaenoic acid, designated shibic acid, was isolated by Ueno and Yonese (495) from bluefin tuna liver oil. The structure of the acid is unknown.

(f) Alkahaenoic Acids, $C_nH_{2n-12}O_2$

Only a few natural alkahaenoic (hexaethenoic, hexaenoic) acids are known, all of which are constituents of marine animal oils. They are normal acids having 22 to 26 atoms in their carbon skeletons. One hexaenoic acid has been synthesized. It contains six conjugated double bonds and corresponds to the formula $CH_3(CH:CH)_6COOH$. The synthesis of this and related highly unsaturated conjugated acids is discussed in Chapter XVIII.

Docosaheptaenoic Acids, $C_{22}H_{32}O_2$. Klenk and co-workers (453) reported the isolation of 4,7,10,13,16,19-docosaheptaenoic acid from brain phosphatides. Hammond and Lundberg (496) reported the isolation of a docosaheptaenoic acid from hog brain lipids. Based on various physical and chemical characteristics including infrared and ultraviolet spectral data they assigned to the acid a structure corresponding to *cis*-4,7,10,13,-

16,19-docosahexaenoic. An acid having the same structure was isolated by Whitcutt (496a) from South African pilchard oil.

In 1938, Farmer and van den Heuvel (497) reported the isolation of a docosahexaenoic acid by molecular distillation of the methyl esters of codliver oil and showed it to be structurally pure and nonconjugated. On complete reduction it yielded behenic (*n*-docosanoic) acid. On the basis of oxidation products of the methyl ester they deduced that the acid contained four $\text{:CHCH}_2\text{CH:}$ groups and one $\text{:CH(CH}_2)_2\text{CH:}$ group between the two terminal groups, $\text{:CH}_3\text{CH:}$ and $\text{:CH(CH}_2)_2\text{COOH}$. On the basis of their results five structures appeared possible but they were unable to decide which one was most probably correct. The five structures fitting the experimental data corresponded to 4,8,11,14,17,20-, 4,7,11,14,17,20-, 4,7,10,14,17,20-, 4,7,10,13,17,20-, and 4,7,10,13,16,20-docosahexaenoic acid.

In 1942 Matsuda (488) reported the isolation of a docosahexaenoic acid from fish oil which he believed to be clupanodonic acid, the structure of which corresponded to either 4,8,12,15,18,21- or 4,8,11,14,17,20-docosahexaenoic. The latter structure is the same as one of those proposed by Farmer and van den Heuvel (497) for the acid isolated from codliver oil.

Tetracosahexaenoic Acids, $\text{C}_{24}\text{H}_{36}\text{O}_2$. In 1934 Toyama and Tsuchiya (498) reported the isolation of nisinic acid from Japanese sardine oil. They established the structure of the acid to be 4,8,12,15,18,21-tetracosahexaenoic.

Hexacosahexaenoic Acids, $\text{C}_{22}\text{H}_{32}\text{O}_2$. In 1936 Ueno and Yonese (495) reported the presence of a hexacosahexaenoic acid in the highly unsaturated acid fraction of the liver oil of the bluefin tuna. They named it thynnic acid but did not determine its structure.

(g) *Monoalkylalkenoic Acids*

The isolation from the lipids of tubercle bacilli of various alkyl-branched unsaturated acids, especially alkylalkenoic acids, such as C_{27} -phthienoic acid (499) or mycolipenic acid (500), stimulated the synthesis of a considerable number of related acids. In general, the natural products have been shown to be polymethyl-branched α,β -unsaturated acids, i.e., polymethyl-2-alkenoic acids. Because of the difficulties inherent in obtaining sufficient quantities of the natural acids for establishing their structures by means of degradative reactions, numerous synthetic acids have been prepared for use in model degradative studies and for biological testing. For the most part the synthetic acids prepared for these purposes are

α,β -unsaturated and contain one to three methyl side chains. A few acids having a double bond elsewhere than the α,β -position, and with side chains other than methyl, have been prepared. The lowest members of the methylalkenoic acid series have been known for many years and a few of them are industrially important. A few others have been obtained by degradation of natural substances, for example, terpene bodies.

Data with reference to the more important monoalkylalkenoic acids have been assembled in Table 20.

Methylpropenoic (Methacrylic) Acid, $C_4H_6O_2$. The lowest member of the alkyl-substituted alkenoic (olefinic) series of acids is 2-methylpropenoic (α -methacrylic) acid, $CH_2:C(CH_3)COOH$. It is not known to occur in nature. This industrially important acid is manufactured by the accelerated oxidation of methacrolein (501), hydrolysis of acetone cyanohydrin (502), oxidation of methyl vinyl ketone with metal hypochlorites (503), and the dehydration of α -hydroxyisobutyric acid with phosphorus pentoxide (504).

Methacrylic acid is a liquid at ordinary temperatures but at lower temperatures is a solid melting at $15-16^\circ C$. It boils at 163° at 760 mm. and at $81^\circ C$. at 30 mm. pressure. Its density is 1.0153_d^{20} and refractive index 1.4314_d^{20} . It is soluble in water, ethanol, and diethyl ether. It has a characteristic biting odor, is a stronger acid than acetic, is very corrosive, and requires careful handling.

Methacrylic acid undergoes reactions characteristic of compounds with two functional groups, the double bond and the carboxyl. These reactions include normal neutralization and reduction with sodium amalgam to isobutyric acid. Halogens and halogen acids do not add in accordance with Markownikoff's rule, but in the opposite manner which is characteristic of unsaturation conjugated with a carbonyl group. It adds hydriodic or hypochlorous acid to give 2-iodo- or 2-chloro-1-hydroxyisobutyric acid. Fusion with potassium hydroxide yields propionic acid.

Methacrylic acid, like acrylic acid, readily undergoes polymerization to various degrees forming products of considerable commercial importance. In the form of polymeric acids and salts methacrylic acid is used as a water-soluble thickening agent, as a constituent of varnishes and lacquers, auxiliaries in printing pastes, in dyeing, binders for pastes, artificial rubber, and germicides.

Although methacrylic acid is available commercially in anhydrous form, it is commonly used in the form of a polymerized product. It is also used in the form of the methyl ester (methyl methacrylate). The ester polymerizes to a hard, transparent, optically clear product with excellent

TABLE 20
 Monoalkylalkenoic Acids

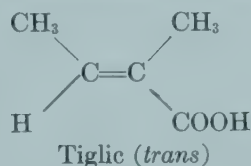
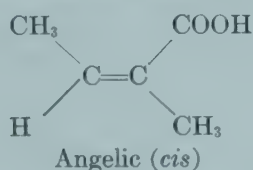
Systematic name	Molecular formula	Structural formula, R—COOH	Formula weight	M.p., °C	B.p., °C./mm. ^a
2-Methylpropenoic ^b	C ₄ H ₆ O ₂	CH ₂ :C(CH ₃)—	86.09	16	163
<i>cis</i> -2-Methyl-2-butenic ^c	C ₅ H ₈ O ₂	CH ₃ CH:C(CH ₃)—	100.11	45	185
<i>trans</i> -2-Methyl-2-butenic ^d	C ₅ H ₈ O ₂	CH ₃ CH:C(CH ₃)—	100.11	65.5	198.5
3-Methyl-2-butenic ^e	C ₅ H ₈ O ₂	(CH ₃) ₂ C:CH—	100.11	70	195
<i>trans</i> -2-Methyl-2-pentenoic	C ₆ H ₁₀ O ₂	CH ₃ CH ₂ CH:C(CH ₃)—	114.14		123/29.5
4-Methyl-3-pentenoic ^f	C ₆ H ₁₀ O ₂	(CH ₃) ₂ C:CH(CH ₂)—	114.14		207
<i>cis</i> -2-Methyl-2-hexenoic	C ₇ H ₁₂ O ₂	(CH ₃)(CH ₂) ₂ CH:C(CH ₃)—	128.17		110/10
<i>trans</i> -2-Methyl-2-hexenoic	C ₇ H ₁₂ O ₂	(CH ₃)(CH ₂) ₂ CH:C(CH ₃)—	128.17		118/11
<i>trans</i> -2-Methyl-2-heptenoic	C ₈ H ₁₄ O ₂	(CH ₃)(CH ₂) ₃ CH:C(CH ₃)—	142.19		129/11
3-Methyl-2-nonenoic	C ₁₀ H ₁₈ O ₂	CH ₃ (CH ₂) ₅ C(CH ₃):CH—	170.24		113/1
3-Methyl-2-nonenic	C ₁₀ H ₁₈ O ₂	CH ₃ (CH ₂) ₄ CH:C(CH ₃)CH ₂ —	170.24		109/1.5
5-Methyl-2-hendecenoic	C ₁₂ H ₂₂ O ₂	CH ₃ (CH ₂) ₅ CH(CH ₃)CH ₂ CH:CH—	198.30		158/5
2-Methyl-2-dodecenoic	C ₁₃ H ₂₄ O ₂	CH ₃ (CH ₂) ₈ CH:C(CH ₃)—	212.32	33	
(-)-5-Methyl-2-tridecenoic	C ₁₄ H ₂₆ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)CH ₂ CH:CH—	226.35		168/2.5
2-Methyl-9-octadecenoic ^g	C ₁₉ H ₃₆ O ₂	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₆ CH(CH ₃)—	296.48		194/1
2-Ethyl-9-octadecenoic ^g	C ₂₀ H ₃₈ O ₂	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₆ CH(C ₂ H ₅)—	310.50		196/0.5
2-Propyl-9-octadecenoic ^g	C ₂₁ H ₄₀ O ₂	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₆ CH(C ₃ H ₇)—	324.53		206/0.5
2-Methyl-2-eicosenoic	C ₂₁ H ₄₀ O ₂	CH ₃ (CH ₂) ₁₆ CH:C(CH ₃)—	324.53	66.3	
2-Methyl-2-hexacosenoic	C ₂₇ H ₅₂ O ₂	CH ₃ (CH ₂) ₂₂ CH:C(CH ₃)—	408.69	85.4	

^a Where no pressure is indicated it is atmospheric.^b Common name methacrylic.^c Common name angelic.^d Common name tiglic.^e Also called β , β -dimethylacrylic.^f Common name pyrotartaric.^g K. E. Schulte, W. Weisskopf, and I. Kirschner, *Z. physiol. Chem.*, **288**, 69–82 (1951).

resistance to water and various organic solvents. Methacrylate esters are used as pour point depressants for waxy oil stocks.

Methylbutenoic Acids, $C_5H_8O_2$. Two position isomers of methylbutenoic acid are theoretically possible and both are known. They are 2-methylbutenoic acid, which is capable of existing in two geometrically isomeric forms, and 3-methylbutenoic acid, which has only one form. Both forms of 2-methylbutenoic acid, namely, angelic and tiglic acid, are found in nature. The 3-isomer has not been found in nature.

2-Methyl-2-butenic acid, $CH_3CH:C(CH_3)COOH$, occurs in two stereoisomeric forms which have been designated angelic (*cis*) acid and tiglic (*trans*) acid. They have also been called α -methylisocrotonic acid and α,β -dimethylacrylic acid, respectively. Spatially they may be represented as illustrated below. Although the assignment of the respective



structures to angelic and tiglic acids appears to be firmly established (505), Cason and Kalm (506) reported various discrepancies when the ultraviolet spectral data of these two acids were compared with those for higher members of the series.

Angelic acid occurs in the form of an ester in angelica root (*Angelica archangelica*) and in Roman camomile oil. It crystallizes in the form of monoclinic prisms melting at 45° C. and boils at 185° C. In the liquid state at 47° C. the acid has a density of 0.983 and a refractive index of 1.4434. It is slightly soluble in water, soluble in ethanol, and very soluble in diethyl ester.

Tiglic acid has been isolated from the seed oil and the roots of *Croton tiglium* and from Roman camomile oil. It is obtained as a fission product of many different natural products (saponins, veratrine, etc.). It has been reported (507) to occur along with *n*-valeric acid as a metabolic product of bacteria-free *Ascaris*. It crystallizes in the form of triclinic prisms melting at 64.5° C. and boils at 198.5° C. In the liquid state at 81° C. it has a refractive index of 1.4342. It is slightly soluble in cold water, very soluble in hot water, soluble in ethanol, and very soluble in diethyl ether.

Cason and Kalm (506) reported a recent synthesis in which they obtained tiglic acid (m.p. 65.5 – 66.5° C.) in 53% yield. The product was converted to 2,3-dibromotiglic acid by the addition of bromine and de-

hydrohalogenated with potassium *tert*-butoxide to give β -bromoangelic acid, which was then reduced with sodium amalgam to angelic acid (m.p. 44.9–46.0° C.).

Angellic acid is more highly dissociated ($k_a 5 \times 10^{-5}$) than tiglic acid ($k_a 9.6 \times 10^{-6}$), and the former has a slower rate of esterification with methanol than the latter. It also has a higher heat of combustion (635 kg.cal./mole) than tiglic acid (627 kg.cal./mole). It also is the more labile of the two forms and on warming or treatment with sulfuric acid it passes to the more stable tiglic acid.

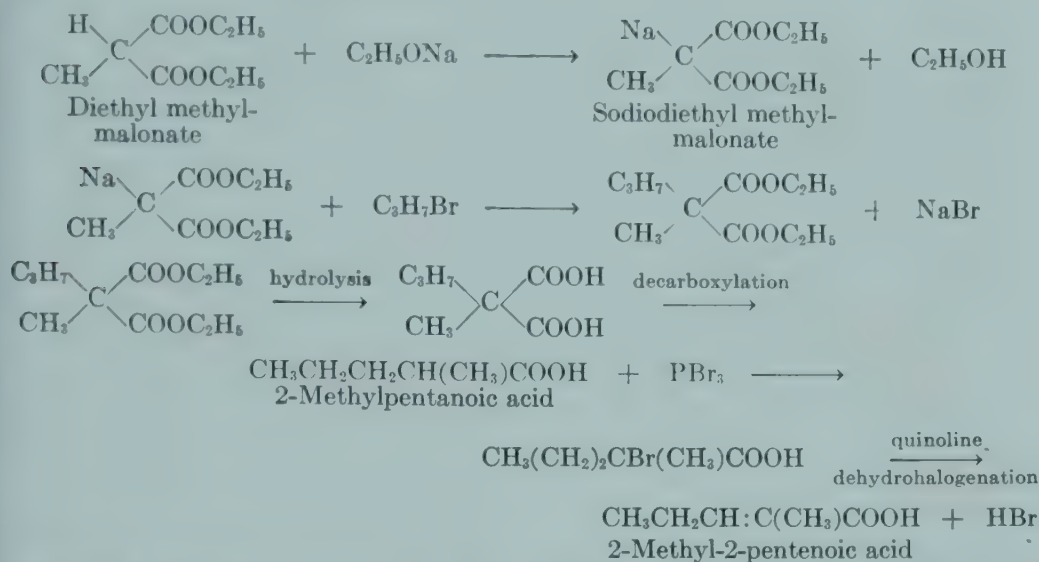
3-Methylbutenoic (β,β -dimethylacrylic) acid, $(\text{CH}_3)_2\text{C}:\text{CHCOOH}$, is not found in nature. It can be synthesized (a) from acetone and malonic acid, (b) dehydrohalogenation of 2-bromoisovaleric acid, and (c) by dehydrating 2-hydroxyisovaleric acid obtained from acetone, bromoacetic acid, and zinc (Reformatsky reaction). The last mentioned reaction is a general one for the preparation of α,β -unsaturated acids of the type $\text{RR}':\text{CH}''\text{COOH}$. β,β -Dimethylacrylic acid can also be prepared from diacetone alcohol by dehydrating the latter in the presence of a trace of iodine by slowly distilling the volatile reaction product, namely, mesityl oxide, which in reality is an α,β -unsaturated ketone. Treatment of the ketone with sodium hypochlorite converts it in good yield to 3-methylbutenoic acid.

β,β -Dimethylacrylic acid is a crystalline solid melting at 70° and boiling at 195° C. It exhibits the reaction of its lower homologs and, in addition, an enhanced activity of the hydrogen atoms of the terminal methyl groups which results from their juxtaposition to the conjugated unsaturation of the molecule.

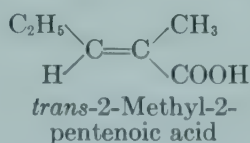
Methylpentenoic Acids, $\text{C}_6\text{H}_{10}\text{O}_2$. The isolation of the physiologically active C_{27} -phthienoic acid from the lipids of the tubercle bacillus by Cason and Sumrell (499) in 1951 and the assignment of a partial structure to it, including the features of a 2-methyl-2-alkenoic acid, led Cason and co-workers to an extensive study of the methods of preparation of acids of this type. The series included many members from 2-methyl-2-butenic acid to 2-methyl-2-hexacosenoic acid. Many of the acids had never been prepared before and a number of them were prepared by more than one method.

trans-2-Methyl-2-pentenoic acid, $\text{CH}_3\text{CH}_2\text{CH}:\text{C}(\text{CH}_3)\text{COOH}$, was prepared by Cason and Kalm (506) from the corresponding saturated acid. The saturated acid was prepared by alkylation of diethyl methylmalonate with propylbromide to yield 2-methylpentanoic (α -methylcaproic) acid, followed by bromination to give 2-methyl-2-bromopentanoic

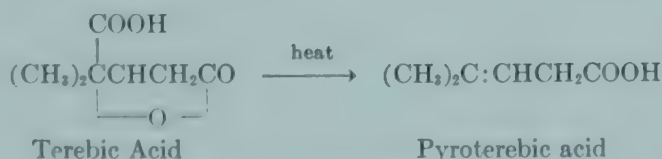
acid which was dehydrohalogenated with quinoline to give the desired *trans*-2-methyl-2-pentenoic acid. The method is a general one for the preparation of α -branched-chain alkenoic acids. The reactions involved may be represented as follows:



trans-2-Methyl-2-pentenoic acid boils at 123–125° C. at 29.5 mm. pressure. It has a refractive index of 1.4581_D²⁵. On the basis of the ultraviolet and infrared spectra of this acid and other higher homologs it was assigned the spatial configuration shown below.



4-Methyl-3-pentenoic (pyroterebic) acid, $(\text{CH}_3)_2\text{C}:\text{CHCH}_2\text{COOH}$, occurs in nature esterified with a diterpene alcohol in the milky sap of *Calotropis procera*. Pyroterebic acid (b.p. 207° C.) is obtained by heating terebic (2,2-dimethylparaconic) acid to a temperature at which it loses a molecule of carbon dioxide.



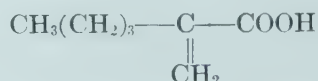
Terebic acid is obtained as a product of oxidation of α -terpineol and it has been synthesized from bromosuccinic ester, zinc, and acetone; also

from α -bromo- β -dimethylglutaric ester by removing hydrogen bromide by means of alcoholic potash.

Methylhexenoic Acids, $C_7H_{12}O_2$. Both the *cis*- and *trans*-2-methyl-2-hexenoic acids, $CH_3(CH_2)_2CH:C(CH_3)COOH$, have been prepared. Cason and Kalm (506) prepared the *trans*-acid by the method described above for the next lower homolog except that the sodiodiethyl methylmalonate was alkylated with butylbromide to give 2-methylhexanoic acid which on α -bromination followed by dehydrohalogenation with quinoline gave the desired *trans*-2-methyl-2-hexenoic acid. The acid is liquid boiling at $118\text{--}119^\circ\text{C}$. at 11 mm. pressure. It has a refractive index of 1.4602_D^{25} , an absorption maximum at $217\text{ m}\mu$; and extinction maximum at $13,580$.

The corresponding methyl ester is a liquid boiling at $81.5\text{--}82.0^\circ\text{C}$. at 30 mm. pressure and has a refractive index of 1.4420_D^{25} .

The authors prepared the isomeric 2-methylenehexanoic acid,



by dehydrohalogenation of the ester of 2-bromo-2-methylhexanoic acid with potassium *tert*-butoxide. The acid is a liquid boiling at 111°C . at 10 mm. pressure. It has a refractive index of 1.4435_D^{25} .

cis-2-Methyl-2-hexenoic acid was prepared by the same authors, starting with 2-hexanone which was prepared by reaction of dibutylleadmium with acetyl chloride. The saturated ketone was converted to 2-hydroxy-2-methylhexanoic acid by the method of Lucas and Prater (508). The hydroxymethylhexanoic acid was pyrolyzed and the products distilled to obtain the desired *cis*-2-methyl-2-hexenoic acid. The acid is a liquid boiling at 110°C . at 10 mm. pressure and has a refractive index of 1.4525_D^{25} . The corresponding methyl ester is a liquid with a refractive index of 1.4333_D^{25} .

The ultraviolet and infrared spectra of each stereoisomeric acid were determined.

Methylheptenoic Acids, $C_8H_{16}O_2$. *trans*-2-Methyl-2-heptenoic acid, $CH_3(CH_2)_3CH:C(CH_3)COOH$, was prepared by Cason and Kalm (506) by the method described above for preparing the corresponding 2-methyl-2-pentenoic acid except that alkylation was carried out with *n*-amyl bromide ($C_5H_{11}Br$) to yield 2-methylheptanoic acid which on α -bromination followed by quinoline dehydrohalogenation of the bromo derivative gave the desired *trans*-2-methyl-2-heptenoic acid. The acid is a liquid boiling at $129.5\text{--}131^\circ\text{C}$. at 11 mm. pressure and has a refractive index of 1.4605_D^{25} .

Methylnonenoic Acids, $C_{10}H_{18}O_2$. 3-Methyl-2-nonenoic acid, $CH_3-(CH_2)_5C(CH_3):CHCOOH$, and 3-methyl-3-nonenoic acid, $CH_3(CH_2)_4-CH:C(CH_3)CH_2COOH$, were prepared by Cason and Sumrell (509) from ethyl 3-hydroxy-3-methylnonanoate which was dehydrated with either iodine or thionyl chloride and pyridine to give a mixture of two parts of ethyl 3-methyl-2-nonenoate and one part of ethyl 3-methyl-3-nonenoate. The two esters, which boil 10 degrees apart at 5 mm. pressure, were separated by fractional distillation. The separated esters were saponified and the free acids purified.

3-Methyl-2-nonenoic acid is a liquid boiling at $113-114^\circ C.$ at 1.0 mm. pressure and has a refractive index of 1.4648_D^{25} . 3-Methyl-3-nonenoic acid is a liquid boiling at $109-111^\circ C.$ at 1.5 mm. pressure and has a refractive index of 1.4522_D^{25} . The ultraviolet spectrum of each acid was determined.

Methylhendecenoic Acids, $C_{12}H_{22}O_2$. 5-Methyl-2-hendecenoic acid, $CH_3(CH_2)_5CH(CH_3)CH_2CH:CHCOOH$, was prepared by Cason *et al.* (510) from the corresponding saturated acid via the α -bromo acid which was dehydrohalogenated with potassium *tert*-butoxide. The acid boils at $158-161^\circ C.$ at 5 mm. pressure and has a refractive index of 1.4587_D^{25} . Its ultraviolet absorption spectrum was determined. In the course of the preparation of this acid the authors also prepared 2-hexacosenoic acid and its methyl ester, 2-dodecenoic acid, 3-methylnonanoic acid, and 5-methylhendecanoic acid and described their properties.

Methyldodecenoic Acids, $C_{13}H_{24}O_2$. 2-Methyl-2-dodecenoic acid, $CH_3(CH_2)_8CH:C(CH_3)COOH$, was prepared by Cason *et al.* (511) via 5-methyldodecanoic acid (b.p. $159.5-160.5^\circ C.$, n_D^{25} 1.4401, m.p. $24^\circ C.$). The methyl ester of the saturated acid was brominated with *N*-bromosuccinimide and the bromo ester dehydrohalogenated with quinoline at $150^\circ C.$ 2-Methyl-2-dodecenoic is a crystalline solid melting at $33^\circ C.$ and has a refractive index of 1.4698_D^{25} . Its ultraviolet spectrum was determined.

In the course of the preparation of this acid the authors also prepared 2-methyldodecanoic acid and its methyl ester and 2-methylenedodecanoic acid.

Methyltridecenoic Acids, $C_{14}H_{26}O_2$. (—)-5-Methyl-2-tridecenoic acid, $CH_3(CH_2)_7CH(CH_3)CH_2CH:CHCOOH$, was prepared by Cason *et al.* (512) by α -bromination of (—)-5-methyltridecanoic acid followed by dehydrohalogenation with potassium *tert*-butoxide. The saturated acid was prepared by hydrolysis and decarboxylation of dimethyl (+)-4-methyl-dodecane-1,1-dicarboxylate previously prepared by alkylation of

dimethyl malonate with (+)-bromo-3-methylhendecane. (—)-5-Methyl-2-tridecenoic acid is a liquid boiling at 168–170° C. at 2.5 mm., refractive index 1.4620_D²⁵, density 0.908²⁵, $[\alpha]_D^{23}$ –1.370, $[M]_D^{23}$ –3.10.

Methyleicosenoic Acids, C₂₁H₄₀O₂. 2-Methyl-2-eicosenoic acid, CH₃(CH₂)₁₆CH:C(CH₃)COOH, was prepared by Cason and Kalm (513) by α -bromination of the corresponding saturated acid with phosphorus tribromide followed by dehydrohalogenation with quinoline. 2-Methyl-2-eicosenoic acid is a crystalline solid melting at 66.3–67.6° C. The corresponding saturated acid, 2-methyleicosanoic, (m.p. 61.5–62.0° C.) was prepared by alkylating diethyl methylmalonate with *n*-octadecylbromide in the presence of sodium ethoxide.

Methylhexacosenoic Acids, C₂₇H₅₂O₂. 2-Methyl-2-hexacosenoic acid, CH₃(CH₂)₂₂CH:C(CH₃)COOH, was prepared by Cason and Kalm (513) in the same manner as described above for 2-methyl-2-eicosenoic acid. Diethyl methylmalonate was alkylated with *n*-tetracosyl bromide in the presence of sodium ethoxide to give the corresponding saturated 2-methylhexacosanoate, which was saponified and the free acid brominated in the α -position with phosphorus tribromide, followed by dehydrohalogenation with quinoline to yield the desired acid. 2-Methyl-2-hexacosenoic acid is a crystalline solid melting at 85.4–86.2° C. The corresponding saturated acid, 2-methylhexacosanoic, melted at 73.5–75.0° C.

(h) Polyalkylalkenoic Acids

Interest in the polyalkylalkenoic acids resulted from the isolation of an acid of this type from the lipids of the tubercle bacillus. Owing to the difficulty in obtaining the acid (C₂₇-phthienoic) in quantity and in rigidly pure form, recourse was had to the synthesis of type compounds for comparison with the natural product. Both optically active and racemic compounds were synthesized. Data with respect to these polyalkylalkenoic acids have been assembled in Table 21.

Teracrylic Acid, C₇H₁₂O₂. Teraerylic or 3,4-dimethyl-3-pentenoic acid, (CH₃)₂C:C(CH₃)CH₂COOH, is obtained by heating terpenylic acid, one of the oxidation products of commercial terpineol. The product is a liquid boiling at 218° C.

Dimethyldecanoic Acids, C₁₂H₂₂O₂. DL-2,4-Dimethyl-2-decenoic acid, CH₃(CH₂)₅CH(CH₃)CH:C(CH₃)COOH, was prepared by Cason and Allen (514) from the corresponding 2,4-dimethyldecanoic acid by α -bromination followed by dehydrohalogenation with quinoline. The acid is a liquid boiling at 155° C. at 5.5 mm. pressure and has a refractive index of 1.4621_D²⁵.

TABLE 21
Polyalkylalkenoic Acids

Systematic name	Molecular formula	Structural formula, R—COOH	Formula weight	M.p., ° C. or b.p., ° C./mm.
3,4-Dimethyl-3-pentenoic ^a	C ₇ H ₁₂ O ₂	(CH ₃) ₂ C:C(CH ₃)CH ₂ —	128.66	218/760
m-2,4-Dimethyl-2-decenoic	C ₁₂ H ₂₂ O ₂	CH ₃ (CH ₂) ₅ CH(CH ₃)CH:C(CH ₃)—	198.30	155/5.5
5,9-Dimethyl-2-decenoic ^b	C ₁₂ H ₂₂ O ₂	CH ₃ CH(CH ₃)(CH ₂) ₃ CH(CH ₃)CH ₂ CH:CH—	198.30	151/3
1(+)-2,4-Dimethyl-2-dodecenoic	C ₁₄ H ₂₆ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)CH:C(CH ₃)—	226.35	liq.
1(+)-2,5-Dimethyl-2-tridecenoic	C ₁₅ H ₂₈ O ₂	CH ₃ (CH ₂) ₇ CH(CH ₃)CH ₂ CH:C(CH ₃)—	240.37	176/5.5
2,5-Dimethyl-2-heptadecenoic	C ₁₉ H ₃₆ O ₂	CH ₃ (CH ₂) ₁₁ CH(CH ₃)CH ₂ CH:C(CH ₃)—	296.48	liq.
2,2-Dimethyl-11-eicosenoic ^c	C ₂₂ H ₄₂ O ₂	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₈ C(CH ₃) ₂ —	338.56	240/4
trans-2,4(n)-Dimethyl-2-heneicosenoic	C ₂₃ H ₄₄ O ₂	CH ₃ (CH ₂) ₁₆ CH(CH ₃)CH:C(CH ₃)—	352.58	46(49.6) ^d
trans-2,5(n)-Dimethyl-2-heneicosenoic	C ₂₃ H ₄₄ O ₂	CH ₃ (CH ₂) ₁₅ CH(CH ₃)CH ₂ CH:C(CH ₃)—	352.58	39.6
2,4-Dimethyl-2-pentacosenoic	C ₂₇ H ₅₂ O ₂	CH ₃ (CH ₂) ₂₀ CH(CH ₃)CH:C(CH ₃)—	408.69	69.5
trans-2,4-Dimethyl-13-n-aryl-2-eicosenoic ^e	C ₂₇ H ₅₂ O ₂	CH ₃ (CH ₂) ₆ CH(C ₆ H ₁₁)(CH ₂) ₈ CH(CH ₃)CH:C(CH ₃)—	408.69	
2,4,6-Trimethyl-2-tetracosenoic ^f	C ₂₇ H ₅₂ O ₂	CH ₃ (CH ₂) ₁₇ CH(CH ₃)CH ₂ CH(CH ₃)CH:C(CH ₃)—	408.69	

^a Trivial name, tetracrylic acid.^b F. L. Breusch and F. Baykut, *Rev. Fac. Sci. Univ. Istanbul*, **16A**, 137-143 (1950).^c N. P. Bau-Hoi and P. Cagniant, *Z. physiol. Chem.*, **279**, 76-86 (1943).^d Dimorphs.^e Trivial name, C₂₇-phthienoic acid.^f Trivial name, mycolipenic acid.

The saturated acid was prepared from 3-methylnonanoic acid which was converted to the silver salt, treated with bromine in carbon tetrachloride solution, and decarboxylated to give 1-bromo-2-methyloctane. Diethyl methylmalonate was reacted with sodium ethoxide in absolute ethanol followed by alkylation with bromide. The product was saponified and decarboxylated to yield 2,4-dimethyldecanoic acid. The saturated acid is a liquid boiling at 165.5° C. at 13 mm. and has a refractive index of 1.4382_D²⁵.

Dimethyldodecenoic Acids, C₁₄H₂₆O₂. L-(+)-2,4-Dimethyl-2-dodecenoic acid, CH₃(CH₂)₇CH(CH₃)CH:C(CH₃)COOH, was prepared by Cason and Allen (514) from the corresponding saturated acid, (+)-2,4-dimethyldodecanoic, by α-bromination of the latter followed by dehydrobromination with quinoline at 160–170° C. The unsaturated acid is a liquid having a density of 0.901²⁵, refractive index 1.4636_D²⁵, specific rotation [α]_D²⁵ + 39.65°, molecular rotation [M]_D²⁵ + 89.76°, and exhibiting a maximum absorption in the ultraviolet at 217 mμ.

The intermediate saturated acid was prepared by alkylation of diethyl methylmalonate with (+)-1-bromo-2-methyldecane which gave diethyl L-(+)-4-methyldodecane-2,2-dicarboxylate. The disubstituted malonic ester was saponified and decarboxylated by heating to 180° C. The (+)-2(DL),4(L)-dimethyldodecanoic acid is a liquid boiling at 172.5–173.5° C. at 7.5 mm. It has a density of 0.878²⁵, refractive index 1.4421_D²⁵, + 2.92°, and a molecular rotation [M]_D²⁵ + 6.68°.

Dimethyltridecenoic Acids, C₁₅H₂₈O₂. L-(+)-2,5-Dimethyl-2-tridecenoic acid, CH₃(CH₂)₇CH(CH₃)CH₂CH:C(CH₃)COOH, was prepared by Cason *et al.* (512) via the following route. (+)-1-Bromo-3-methylhendecane was prepared in optically pure form and used to alkylate diethyl methylmalonate. The diethyl (+)-5-methyltridecane-2,2-dicarboxylate obtained by this reaction was saponified and decarboxylated to give (+)-2(DL)-dimethyltridecanoic acid. The saturated acid is a liquid boiling at 176–177.5° C. at 5.5 mm., density 0.8812²⁷, refractive index 1.4439_D²⁵, [α]_D²⁷ + 1.08°, [M]_D²⁷ + 2.61. The saturated acid was α-brominated with phosphorus tribromide and dry bromine, and the resulting 2-bromo-2-methyl derivative was dehydrohalogenated with quinoline to yield the desired dimethyltridecenoic acid. This acid is a liquid boiling at 149–154° C. at 1 mm., refractive index 1.4435_D²⁵, [α]_D²⁷ + 0.935°, [M]_D²⁷ + 2.24° C.

Dimethylheptadecenoic Acids, C₁₉H₃₆O₂. 2,5-Dimethyl-2-heptadecenoic acid, CH₃(CH₂)₁₁CH(CH₃)CH₂CH:C(CH₃)COOH, was prepared by Cason *et al.* (512) by α-bromination of the corresponding saturated

acid with phosphorus tribromide and dry bromine, followed by dehydrohalogenation of the product of bromination with quinoline. The acid is a liquid with a refractive index 1.4662_D^{25} . The required saturated acid was prepared by the diethyl methylmalonate synthesis described for the preparation of dimethyltridecenoic acid except that 1-bromo-3-methylpentadecane was used as the alkylating agent.

Dimethylheneicosenoic Acids, $C_{23}H_{44}O_2$. Two dimethylheneicosenoic acids, namely, *trans*-2,4(D)-dimethyl-2- and *trans*-2,5(D)-dimethyl-2-heneicosenoic, have been prepared by Ställberg-Stenhagen (515).

trans-2,4(D)-Dimethyl-2-heneicosenoic acid, $CH_3(CH_2)_{16}CH(CH_3)-CH:C(CH_3)COOH$, was prepared via the following reactions:

L(+)-Methyl hydrogen β -methylglutarate was reacted with *n*-heptadecanoic acid in a Kolbe electrolytic synthesis to give the dimorphic (+)-methyl-3(D)-methyleicosanoate (m.p. 30.1 – 30.4° and 21.1 – 21.3° C.) which on hydrolysis yielded (+)-3(D)-methyleicosanoic acid, m.p. 52.2 – 52.4° C., $[\alpha]_D^{23} + 4.00$, $[M]_D^{23} + 13.1^\circ$.

The methyleicosanoic acid was reacted with ethyl hydrogen methylmalonate by anodic synthesis which yielded a mixture of ethyl esters of stereoisomeric 2,4-dimethylheneicosanoic acids and other products. The esters were separated from the reaction mixture by distillation and chromatography on aluminum oxide. The mixed esters were hydrolyzed and the acids α -brominated, converted to the ethyl esters, and the latter dehydrohalogenated. Separation of the unsaturated acid esters by chromatographing the mixture on aluminum oxide gave (–)-ethyl *trans*-2,4(D)-dimethyl-2-heneicosenoate. The ester melts at 23.6 – $24.^\circ$ C., has a molecular rotation in petroleum naphtha $[M]_D^{22} - 84^\circ$ and exhibits maximum absorption in the ultraviolet at $218\text{ m}\mu$. Hydrolysis of the ester gave dimorphic (–)-*trans*-2,4(D)-dimethyl-2-heneicosenoic acid (m.p. 46 – 46.2° and 49.6 – 50.2° C.). In chloroform solution the acid has a specific rotation $[\alpha]_D^{23} - 21.9^\circ$ and a molecular rotation $[M]_D^{23} - 77^\circ$.

trans-2,5(D)-Dimethyl-2-heneicosenoic acid, $CH_3(CH_2)_{15}CH(CH_3)-CH_2CH:C(CH_3)COOH$, was prepared by the following series of reactions:

(+)-3(D)-Methylnonadecanoic acid, $CH_3(CH_2)_{15}CH(CH_3)CH_2COOH$, was prepared by reacting L(+)-methyl hydrogen β -methylglutarate, $HOOC\cdot CH_2CH(CH_3)CH_2COOCH_3$, with palmitic acid by a Kolbe electrolytic synthesis followed by hydrolysis of the resulting ester. The acid was converted to the alcohol, (+)-3(D)-methylnonadecanol-1, by reduction with lithium aluminum hydride. The alcohol was converted to the iodide, (–)-1-iodo-3(D)-methylnonadecane. Ethyl methylmalonate

nate was alkylated with the iodide and the product hydrolyzed which yielded a mixture of diastereoisomeric 2,4(D)-dimethylheneicosanoic acids. The mixture of acids was brominated with dry bromine and red phosphorus and the bromo acids esterified to give a mixture of methyl esters which was dehydrohalogenated with quinoline or tri-*n*-propylamine. The mixture of esters was chromatographed on aluminum oxide.

The desired methyl *trans*-2,5(D)-dimethyl-2-heneicosenate was obtained in 15% yield. At ordinary temperatures the ester is a liquid but at lower temperatures it exists in two dimorphic forms (m.p. 8.0–8.5° and 14° C.). In chloroform solution it has a specific rotation $[\alpha]_D^{23} - 0.7^\circ$ and a molecular rotation $[M]_D^{23} - 2.8^\circ$.

Hydrolysis of the methyl ester yields *trans*-2,5(D)-dimethyl-2-heneicosanoic acid. It is a crystalline solid (m.p. 39.6–40.0°) and in chloroform solution exhibits a specific rotation $[\alpha]_D^{23} \pm 0.00$. It has an absorption maximum in the ultraviolet at 217–218 m μ .

Dimethylpentacosenoic Acids, C₂₇H₅₂O₂. 2,4-Dimethyl-2-pentacosenoic acid, CH₃(CH₂)₂₀CH(CH₃)CH:C(CH₃)COOH, has been prepared by Cason and Allen (514) by α -bromination of the corresponding saturated acid, followed by dehydrobromination with quinoline. The acid is a crystalline solid melting at 69.5–70.3°.

The intermediate saturated acid, 2,4-dimethylpentacosanoic acid, was prepared by alkylation of diethyl methylmalonate with 2-methyl-1-tricosyl bromide prepared by reacting bromine with the silver salt of 3-methyltetracosanoic acid. The saturated 2,4-dimethylpentacosanoic acid melts at 44.5–46.0° C.

Phthienoic (Mycolipenic) Acid, C₂₇H₅₂O₂. In 1951 Cason and Sumrell (499) reported the isolation of a polymethyl-branched unsaturated acid from a preparation of crude methyl phthioate originally obtained by Spielman and Anderson (60) from the lipids of tubercle bacillus. The acid was shown to correspond to the formula C₂₇H₅₂O₂ and was provisionally designated C₂₇-phthienoic acid. It was postulated that the acid contained three branching methyl groups, one attached at the 2-position, a second at the 4- or 5-position, and a third farther removed from the carboxyl group.

Subsequently, Cason *et al.* (512) assigned the second methyl group to the 4-position on the basis of the low molecular rotation of the acid. The molecule was also assigned a *trans*-configuration with respect to the double bond on the basis of comparisons of its infrared and ultraviolet spectra with those for various synthetic methyl-substituted 2-methyl-2-alkenoic acids (506). They assigned to the natural product the partial structure 2-methyl-4,*x*-dimethyl-2-alkenoic acid.

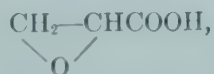
Polgar and Robinson (500), in 1951, reported the isolation of a C_{27} - α,β -unsaturated acid from the lipids of tubercle bacillus. They named the acid mycolipenic acid and subsequently Bailey *et al.* (516) concluded that C_{27} -phthienoic and mycolipenic acids were identical. The following year, Polgar (517), on the basis of results obtained by the oxidative degradation of a mixture of acids containing more than 20 carbon atoms derived from tubercle bacillus lipids, concluded that the principal dextro-rotatory acid in the mixture had an empirical formula corresponding to $C_{27}H_{52}O_2$ and was (+)-2,4,6-trimethyl-2-tetracosenoic acid.

In 1951 Asselineau *et al.* (518) reported the synthesis of a racemic mixture of methyl erythro-2,4,6-trimethyl-2-tetracosenoic acid which they designated methyl C_{27} -phthienoate. The infrared absorption curves of both preparations and of the methyl ester of the naturally occurring C_{27} -phthienoic acid were stated to be identical. Still later, Millin and Polgar (519) reported the synthesis of optically active 2,4,6-trimethyl-2-tetracosenoic and compared its properties with those of natural mycolipenic acid.

Cason and co-workers (520) did not accept the evidence presented up to 1957 for the identity of C_{27} -phthienoic and mycolipenic acids, nor did they agree that the structure of the former corresponded to 2,4,6-trimethyl-2-tetracosenoic acid. They predicated the nonidentity on the lack of homogeneity of the product used by Polgar (517) in his oxidative degradation, the limited data presented by Millin and Polgar (519) for the comparison of their synthetic acid with the natural product, and the evidence which Cason *et al.* (520) deduced for a tentatively proposed complete structure for C_{27} -phthienoic acid, namely, *trans*-2,4-dimethyl-13-n-amy-2-eicosenoic acid.

(i) Hydroxyalkenoic Acids

Hydroxyalkenoic (hydroxyethenoic, hydroxyolefinic) acids are isomeric with aldehydic and ketonic acids and with glycidic acid,



and its homologs. Until the first quarter of the present century the only hydroxyalkenoic acid known to be present in natural fats was ricinoleic (hydroxyoleic). Since then several other homologous acids have been noted. Among them are ambrettolic (16-hydroxy-7-hexadecenoic), 9-hydroxy-12-octadecenoic, and hydroxynervonic (2-hydroxy-15-tetradecenoic). A monohydroxy and a dihydroxy polyunsaturated acid have

TABLE
Hydroxy

Systematic name	Trivial or other name	Molecular formula
3-Hydroxy-2-propenoic	β -Hydroxyacrylic	$C_3H_4O_3$
2-Hydroxy-3-butenic	Vinylglycolic ^b	$C_4H_6O_3$
3-Hydroxy-2-butenic	β -Hydroxyisocrotonic	$C_4H_6O_3$
4-Hydroxy-3-butenic		$C_4H_6O_3$
2-Hydroxy-3-pentenoic	Propenylglycolic	$C_5H_8O_3$
4-Hydroxy-3-pentenoic		$C_5H_8O_3$
4-Hydroxy-4-pentenoic		$C_5H_8O_3$
5-Hydroxy-2,4-pentadienoic		$C_5H_6O_3$
4-Hydroxy-2-hexenoic	Parasorbic	$C_6H_{10}O_3$
3-Hydroxy-4-hexenoic	β -Hydroxyhydrosorbic	$C_6H_{10}O_3$
4-Hydroxy-13-tetradecenoic		$C_{14}H_{26}O_3$
16-Hydroxy-7-hexadecenoic	Ambrettolic	$C_{16}H_{30}O_3$
16-Hydroxy-6-hexadecenoic	Isoambrettolic	$C_{16}H_{30}O_3$
9-Hydroxy-12-octadecenoic		$C_{18}H_{34}O_3$
(+)-12-Hydroxy- <i>cis</i> -9-octadecenoic	Ricinoleic	$C_{18}H_{34}O_3$
(+)-12-Hydroxy- <i>trans</i> -9-octadecenoic	Ricinelaidic	$C_{18}H_{34}O_3$
4-Hydroxy-12-heneicosenoic		$C_{21}H_{40}O_3$
2-Hydroxy-15-tetracosenoic	Hydroxynervonic	$C_{24}H_{46}O_3$
18-Hydroxy-9,11,13-Octadecatrienoic	Kamolenic	$C_{18}H_{30}O_3$
9,14-Dihydroxy-10,12-octadecadienoic		$C_{18}H_{32}O_4$

^a Not known as free acid.^b Also α -hydroxyvinylacetic and ethenylglycolic.^c Trimorphic forms.

also been reported. All of the lower members of the hydroxyalkenoic series are of synthetic origin and none is of commercial importance.

Data with respect to the principal natural and synthetic hydroxyalkenoic acids have been assembled in Table 22.

Hydroxypropenoic (Hydroxyacrylic) Acid, $C_3H_4O_3$. The lowest member of the hydroxyalkenoic series, namely, hydroxypropenoic or β -hydroxyacrylic acid, $HOCH:CHCOOH$, is not known per se, but only in

Structural formula, R—COOH	Formula weight	M.p., ° C.	Derivative, ° C. or ° C./mm.
CH(OH):CH—	88.06	^a	Acetate, b.p. 126/46
CH ₂ :CHCH(OH)—	102.09	40	
CH ₃ C(OH):CH—	102.09	^a	Methylether ester, m.p. 128
CH(OH):CHCH ₂	102.09	^a	Lactone, m.p. 4, b.p. 96/15
CH ₃ CH:CHCH(OH)—	116.11		
CH ₃ C(OH):CHCH ₂ —	116.11	^a	Lactone, m.p. 18, b.p. 167
CH ₂ :C(OH)(CH ₂) ₂ —	116.11	^a	Lactone, b.p. 84/25
CH(OH):CHCH:CH—	114.10		
CH ₃ CH ₂ CHOHCH:CH—	130.14	^a	Lactone, b.p. 221
CH ₃ CH:CHCH(OH)CH ₂ —	130.14		Ethylester, b.p. 100/2
CH ₂ :CH(CH ₂) ₈ CH(OH)(CH ₂) ₂ —	242.35		Lactone, m.p. 26–27
CH ₂ (OH)(CH ₂) ₇ CH:CH(CH ₂) ₅ —	270.40	25	
CH ₂ (OH)(CH ₂) ₈ CH:CH(CH ₂) ₄ —	270.40	71–72	
CH ₃ (CH ₂) ₄ CH:CH(CH ₂) ₂ CH(OH)(CH ₂) ₇ —	298.45		
CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH:CH(CH ₂) ₇ —	298.45	5.0, 7.7, 16.0 ^c	
CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH:CH(CH ₂) ₇ —	298.45	52–53	
CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₇ CH(OH)(CH ₂) ₂ —	340.53		Lactone, m.p. 42
CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₁₂ CH(OH)—	382.61	65	
CH ₂ (OH)(CH ₂) ₃ (CH:CH) ₃ (CH ₂) ₇ —	294.42	77–78, 88–89	
CH ₃ (CH ₂) ₈ CH(OH)(CH:CH) ₂ CH(OH)(CH ₂) ₇ —	312.44	104	

the form of the sodium derivative of its ester. It can be prepared by reaction of formic and acetic acids and sodium in diethyl ether.

Hydroxybutenoic Acids, C₃H₅O₃. Three positionally isomeric hydroxybutenoic acids are theoretically possible and all are known. They are 2-hydroxy-3-butenic, CH₂:CHCHOHCOOH; 3-hydroxy-2-butenic, CH₃:C(OH):CHCOOH; and 4-hydroxy-3-butenic, CH(OH):CHCH₂COOH. The 2-hydroxy acid is also known as α-hydroxyvinylacetic and ethenylglycolic acid; and the 3-hydroxy acid as β-hydroxyisocrotonic acid.

Ethenylglycolic acid can be prepared from acrolein, $\text{CH}_2:\text{CHCHO}$, by way of its cyanhydrin. It is a crystalline solid melting at 40°C . On heating to 190°C . it loses carbon dioxide.

β -Hydroxyisocrotonic acid is known only in the form of its ether acid or ether acid esters, $\text{CH}_3\text{C}(\text{OR}):\text{CHCOOR}$, which are formed by reaction of β -chloroisocrotonic acid or its esters with sodium alcoholates. The methyl ether acid melts at 128°C . and the ethyl ether acid at 137°C .

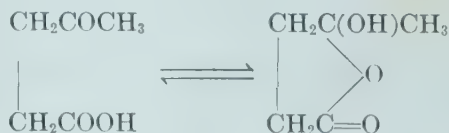
4-Hydroxy-3-butenic acid is known only in the form of its lactone (crotonolactone) which is formed by heating 2,4-dichlorobutyric acid alone or with potassium carbonate. The lactone melts at 4°C . and boils at 96°C . at 15 mm. pressure.

Hydroxypentenoic Acids, $\text{C}_5\text{H}_8\text{O}_2$. The number of theoretically possible isomers of hydroxypentenoic acid is larger than the number actually known.

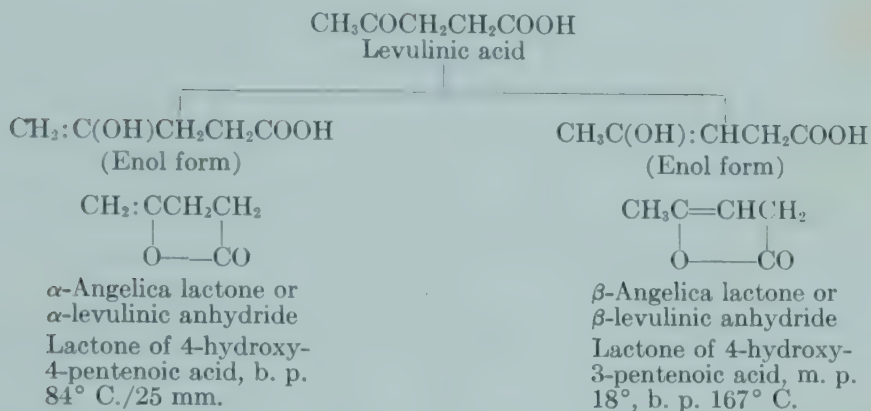
2-Hydroxy-3-pentenoic (propenylglycolic) acid, $\text{CH}_3\text{CH}:\text{CHCH}(\text{OH})\text{COOH}$, is the only hydroxypentenoic acid known to exist in the free state. It can be prepared from crotonaldehyde cyanhydrin. Boiling dilute acids converts the acid directly to levulinic acid, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$.

Two other hydroxypentenoic acids, namely, 4-hydroxy-3-pentenoic, $\text{CH}_3\text{C}(\text{OH}):\text{CHCH}_2\text{COOH}$, and 4-hydroxy-4-pentenoic, $\text{CH}_2:\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{COOH}$, are known only in the form of their gamma lactones or the alpha and beta anhydrides of levulinic acid from which they are obtained by distillation.

Levulinic or γ -ketovaleric acid, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$, is presumed to exist chiefly in the form of its lactone,

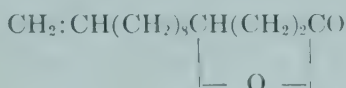


but on prolonged heating as in distillation it is converted into angelica lactones or levulinic anhydrides which are identical with the lactones or anhydrides which would be expected from 4-hydroxy-3- and 4-hydroxy-4-pentenoic acids. The relationship between these compounds is indicated schematically below.



Hydroxytetradecenoic Acids, $\text{C}_{14}\text{H}_{26}\text{O}_3$. 4-Hydroxy-13-tetradecenoic acid was synthesized by Robinson (521) using a variation of the Robinson-Robinson (522) keto acid synthesis. Hendecenyl chloride was condensed with ethyl sodioacetosuccinate and the condensation product was isolated and successively hydrolyzed, first with sulfuric acid, and then with potassium hydroxide. After acidification and steam distillation of the hydrolysate to remove unreacted hendecenoic acid, the 4-keto-13-tetradecenoic acid, $\text{CH}_2:\text{CH}(\text{CH}_2)_8\text{CO}(\text{CH}_2)_2\text{COOH}$, was purified by crystallization from petroleum naphtha.

The keto acid (m.p. 79.5° C.) was reduced with sodium in anhydrous ethanol and subsequently treated with boiling 15% hydrochloric acid which yielded the γ -lactone of 4-hydroxy-13-tetradecenoic acid,



The lactone after crystallization from petroleum naphtha melted at $26\text{--}27^\circ \text{ C.}$

Hydroxyhexadecenoic Acids, $\text{C}_{16}\text{H}_{30}\text{O}_3$. Two hydroxyhexadecenoic acids are known, one of which occurs naturally in the form of its lactone (ambrettolic acid) and a position isomer, isoambrettolic acid which has been prepared synthetically.

Ambrettolic or 16-hydroxy-7-hexadecenoic acid in the form of its lactone, ambrettolide, was first observed by Kerschbaum (523) as a constituent of musk (ambrette) seed oil. The free acid, $\text{HOCH}_2(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$, was prepared from the lactone by Stoll and Gardner (524). On hydrogenation at the double bond, ambrettolic acid is converted into juniperic acid (m.p. 95° C.). Disruptive oxidation at the double bond yields azelaic and pimelic acids.

Isoambrettolic or 16-hydroxy-6-hexadecenoic acid was synthesized by Collaud (525) who first prepared the corresponding lactone, isoambrettolide. The melting point of the acid was reported to be 71–72° C.

Hydroxyoctadecenoic Acids, $C_{18}H_{34}O_3$. Until 1952 ricinoleic or 12-hydroxy-9-octadecenoic acid was the only monohydroxyoctadecenoic acid known with certainty to occur as a constituent of natural fats. In that year Gunstone (526) reported the presence of the isomeric 9-hydroxy-12-octadecenoic acid in the seed fat of a species of *Strophantus*.

9-Hydroxy-12-octadecenoic acid, $CH_3(CH_2)_4CH:CH(CH_2)_2CHOH(CH_2)_7COOH$, was first shown by Gunstone to be a normal constituent of the seed oil of *Strophantus sarmentosus* (family Apocynaceae) in which it forms 6.6% of the total fatty acids. The following year the same author found the acid to be a constituent of the forest form of this species and that it was also present in two other species of *Strophantus*, namely, *S. hispidus* and *S. courmontii*, to the extent of 6.5 to 13.5%.

The structure of the acid was established by hydrogenation to 9-hydroxystearic acid (m.p. 81–82.5° C.) and chromic acid oxidation to 9-ketostearic acid (m.p. 79.5–81° C.). Oxidation of the acid with alkaline potassium permanganate yielded two isomeric 9,12,13-trihydroxystearic acids melting at 108–110° and 148–149° C.

Ricinoleic or (+)-12-hydroxy-*cis*-9-octadecenoic acid, $CH_3(CH_2)_5CHOHCH_2CH:CH(CH_2)_7COOH$, is the oldest and best known hydroxyalkenoic acids. It was first isolated by Saalmüller (527) in 1848 from castor oil in which it is the principal fatty acid constituent. According to Riley (528), Gupta *et al.* (529), and Crossley and Hilditch (530), it constitutes 91 to 95% of the total fatty acids of this oil, but according to other workers (531) it is appreciably less, namely, 80 to 88%. Ricinoleic acid has also been reported by Gurgel and de Amorim (532) to occur in the seed fat of ivory wood (*Agonandra brasiliensis*), and according to Margaillan (533) in the oil of *Wrightia annamensis*, but Hilditch (534) is inclined to doubt its occurrence in these oils. Argemone oil extracted from the seed of *Argemone Mexicana* (Mexican poppy or devil's-fig) was reported by Iyer *et al.* (534a) to contain 9.84% of ricinoleic acid, but a reinvestigation of this oil by Jamieson and Rose (534b) and later by Murari and Roy (534c) failed to reveal the presence of this acid or of any hydroxy component. Jamieson and Rose also failed to confirm the presence of linolenic acid previously reported as a constituent of this oil.

Goldsobel (535) in 1894 showed that ricinoleic acid was 12-hydroxyoleic and in 1899 Maquenne (536) established the position of the double bond

by oxidation to azelaic acid. Ricinoleic acid is represented by two geometric isomers, namely, 12-hydroxy-*cis*-9-octadecenoic acid and 12-hydroxy-*trans*-9-octadecenoic, commonly called ricinelaic acid. The *cis*-acid exhibits three polymorphic crystalline forms melting at 5.0°, 7.7°, and 16.0° C. The *trans*-form, which is produced from the *cis*-form by treatment with the oxides of nitrogen, melts at 52–53° C. The conversion is not complete because the reaction comes to equilibrium in a manner similar to the conversion of oleic to elaidic acid. Both the *cis*- and *trans*-forms are optically active and specific rotations $[\alpha]_D + 7.8^\circ$ and $+ 6.7^\circ$ have been reported for the respective forms. These rotations result from the asymmetry in the molecule at the twelfth carbon atom to which the hydroxyl group is attached.

The principal physical properties of ricinoleic acid have been studied by Hawke (537). Its density at 15.5° C. is 0.940 and refractive index n_D^{20} is 1.4716. It is insoluble in water, completely miscible with ethanol and diethyl ether, and is slightly soluble in chloroform.

Careful oxidation of ricinoleic acid with dilute alkaline potassium permanganate yields two diastereoisomeric 9,10,12-trihydroxystearic acids melting at 112° and 138° (140–142°) C. (538). For reactions of ricinoleic acid under conditions of dehydration and destructive distillation see Chapter X and for sulfation and sulfonation reactions see Chapter XVII.

Ricinoleic acid undergoes esterification by most standard methods and a large number of esters have been prepared and their properties recorded. Esters are formed both at the hydroxyl and the carboxyl group (see Chapter IX). The esters of ricinoleic are readily hydrogenated at the olefinic linkage in the presence of nickel catalysts at a temperature of 130–135° C. to form the corresponding esters of 12-hydroxystearic acid. Alkyl ricinoleates can be reduced to 1,12-octadecanediol at temperatures above 200° C. in the presence of cobalt catalysts or various metal chromites. The same alcohol is produced by the sodium-ethanol reduction process when applied to the esters or glycerides of ricinoleic acid (541). Reduction occurs both at the double bond and the hydroxyl group. By heating under hydrogenation conditions in the presence of cobalt or nickel catalysts, alkyl ricinoleates can be rearranged to alkyl 12-ketostearates (541).

Reaction of the sodium soap, alkyl or glyceryl esters of ricinoleic acid with strong caustic soda yields sebacic acid, $\text{HOOC}(\text{CH}_2)_8\text{COOH}$, and a mixture of methyl *n*-hexyl ketone, $\text{CH}_3\text{CO}(\text{CH}_2)_5\text{CH}_3$, and capryl alcohol (2-octanol), $\text{CH}_3\text{CHOH}(\text{CH}_2)_5\text{CH}_3$.

Two total syntheses of the racemic mixture of *D*- and *L*-ricinoleic acids were reported almost simultaneously by Crombie and Jacklin (542) and

Kendall *et al.* (543). The first synthesis was accomplished by the Grignard reaction between propargyl bromide, $\text{CH}_3\text{C}\equiv\text{CH}_2\text{Br}$, and heptaldehyde (enanthaldehyde), $\text{CH}_3(\text{CH}_2)_5\text{CHO}$, which gave DL-4-hydroxydec-1-yne which was converted into its pyranyl ether. By a chain extension reaction the ether was converted to DL-1-chloro-10-(tetrahydropyranyloxy)-hexadec-7-yne. Hydrolysis, thermal decarboxylation, and destruction of the pyranyl group yielded DL-12-hydroxy-9-octadecenoic (DL-ricinoleic) acid.

The second method (543) required the synthesis of the key intermediate, 1-chloro-10,10-dimethoxydec-7-ene, which was accomplished by reacting 1-iodo-6-hexylene chloride, $\text{Cl}(\text{CH}_2)_6\text{I}$, with monosodium acetylide, $\text{NaC}\equiv\text{CH}$, to give 8-chlorooct-1-yne, $\text{Cl}(\text{CH}_2)_6\text{C}\equiv\text{CH}$. This product was reacted with 2-bromodimethylacetal, $\text{BrCH}_2\text{CH}(\text{OCH}_3)_2$, in lithium-ammonia solution to give 1-chloro-10,10-dimethoxydec-7-yne, $\text{Cl}(\text{CH}_2)_6\text{C}\equiv\text{CCH}_2\text{CH}(\text{OCH}_3)_2$, which was reduced with palladium-hydrogen (Lindlar *cis*-addition) to give the desired intermediate, $\text{Cl}(\text{CH}_2)_6\text{CH}:\text{CHCH}_2\text{CH}(\text{OCH}_3)_2$.

The intermediate was hydrolyzed with aqueous tartaric acid to give the corresponding aldehyde, $\text{Cl}(\text{CH}_2)_6\text{CH}:\text{CHCH}_2\text{CHO}$, which was condensed with *n*-hexylmagnesium bromide, $n\text{-C}_6\text{H}_{12}\text{MgBr}$, to give the unsaturated secondary alcohol, $\text{Cl}(\text{CH}_2)_6\text{CH}:\text{CHCH}_2\text{CHOH}(\text{CH}_2)_5\text{CH}_3$. The chlorine of the secondary alcohol was replaced by iodine by treatment with sodium iodide and the iodide reacted by a malonic ester synthesis to give the corresponding malonate, $(\text{CH}_3\text{OC})_2\text{CH}(\text{CH}_2)_6\text{CH}:\text{CHCH}_2\text{CHOH}(\text{CH}_2)_5\text{CH}_3$, which after hydrolysis and decarboxylation gave the crude methyl ricinoleate. The crude product was fractionally distilled and the colorless ester separated (n_D^{20} 1.4631, m.p. -7° to -5° C.). Saponification of the ester gave ricinoleic acid melting at 3° C. and having a refractive index n_D^{20} 1.4728 compared with a specimen of natural D-ricinoleic acid melting at 5° C. (γ -form); refractive index n_D^{20} 1.4719.

Ricinelaic or (+)-12-hydroxy-*trans*-9-octadecenoic is the *trans*-form of ricinoleic acid and is prepared from the latter by treatment with the oxides of nitrogen. It was first prepared by Playfair (544) in 1846 by the action of nitrous acid on ricinoleic acid. It was known previous to this time in the form of elaidinized castor oil which had been prepared by Boudet (545) as early as 1832. The acid can be prepared from elaidinized castor oil by saponification.

Ricinelaic acid melts at $52\text{--}53^\circ$ C. and is optically active, $[\alpha]_D^{20} + 6.7^\circ$ (in ethanol). Oxidation with dilute alkaline potassium permanganate produces two diastereoisomeric 9,10,12-trihydroxystearic acids melting at 87° and 110° C. (538).

Hydroxyheneicosenoic Acids, $C_{21}H_{40}O_3$. The only hydroxyheneicosenoic acid reported to date is 4-hydroxy-12-heneicosenoic, $CH_3(CH_2)_7CH:CH(CH_2)_7CHOH(CH_2)_2COOH$, which was prepared by Robinson (521) in the form of its γ -lactone. The synthesis followed that described for the preparation of hydroxytetradecenoic acid except that elaidyl chloride was used as the starting material instead of hendecenyl chloride. Condensation of elaidyl chloride with sodioacetosuccinate yielded 4-keto-12-heneicosenoic acid, which on reduction of the keto group with sodium and ethanol gave the corresponding lactone melting at $42^\circ C$.

Hydroxytetracosenoic Acids, $C_{24}H_{46}O_3$. Hydroxynervonic or 2-hydroxy-15-tetracosenoic acid, $CH_3(CH_2)_7CH:CH(CH_2)_{12}CHOHCOOH$, was first prepared by Klenk (546) from a cerebroside fraction partially soluble in petroleum naphtha. It is a white crystalline solid melting at $65^\circ C$., soluble in diethyl ether, chloroform, ethanol, and acetone. It has a specific rotation in pyridine $[\alpha]_D^{20} + 2.87^\circ$ but is reported (547) to exhibit a levorotation in chloroform. The sodium salt is soluble in warm methanol, ethanol, and water, and the lead salt is insoluble in diethyl ether.

The structure of hydroxynervonic acid was established by hydrogenation to cerebronic or 2-hydroxytetracosanoic acid and by ozonolysis which yielded pelargonic acid.

Hydroxyoctadecatrienoic (Kamolenic) Acid, $C_{18}H_{30}O_3$. Kamolenic (hydroxyeleostearic) or 18-hydroxy-9,11,13-octadecatrienoic acid, $HO-CH_2(CH_2)_3(CH:CH)_3(CH_2)_7COOH$, is a primary constituent of kamela (*Mallotus Philippinensis*) oil (548,549). It comprises up to 60% of the total fatty acids of this oil; the remainder consists of oleic, linoleic, lauric, myristic, palmitic, and less than 1% of stearic acid (550).

When first isolated (548) kamolenic acid was presumed to be either 18-hydroxy-9,13,15- or 18-hydroxy-9,12,14-octadecatrienoic acid. Puntambekar (551) postulated that the new acid was a keto compound, but Calderwood and Gunstone (552), Gupta *et al.* (553), and others showed that it was 18-hydroxy-9,11,13-octadecatrienoic acid.

Like eleostearic and licanic acids, kamolenic acid exists in two geometrically isomeric forms (553). The alpha or natural form melts at $77-78^\circ C$. and the beta or isomerized form at $88-89^\circ C$. When completely hydrogenated both forms are converted to 18-hydroxystearic acid (550). Infrared absorption spectra of the two isomers, their acetyl derivatives, and maleic anhydride adducts led Gupta and Aggarwal (554) to conclude that α -kamolenic acid has a *cis*-9,*trans*-11,*trans*-13-structure and β -kamolenic acid an all *trans*-configuration. These structures have been

confirmed by Ahlers and Gunstone (555), Crombie and Taylor (556), and others.

While still in the seed, kamolenic acid tends to undergo polymerization, the product of which appears as an insoluble gelatinous mass during saponification of the oil. It has been postulated that polymerized product is an estolide- or lactide-type condensation product (557).

Dihydroxyoctadecadienoic Acid, $C_{18}H_{32}O_4$. A very small proportion of 9,14-dihydroxy-10,12-octadecadienoic acid, $CH_3(CH_2)_3CHOHCH:CH-CH:CHCH(OH)(CH_2)_7COOH$, was found by Davis *et al.* (558) to be present in tung oil fatty acids. The acid melts at $104-104.5^\circ C$. It is believed to be a product of autoxidation rather than a natural constituent of tung oil.

(j) Ketoalkenoic Acids

Ketoalkenoic acids are rarely found as constituents of natural fats. The only acid of this type which has been isolated from a seed oil is licanic or ketoelostearic which occurs in the seed oils of several species of *Licania* and *Parinarium* indigenous to the tropics.

A number of ketoalkenoic acids have been prepared synthetically but the series is far from complete. Most synthetic acids of this type belong to the 4-keto-2-alkenoic series. Of the known ketoalkenoic acids only licanic has attained commercial importance.

Data referring to the principal ketoalkenoic acids have been assembled in Table 23.

Ketoalkenoic Acids, $C_5H_8O_3$ to $C_{13}H_{22}O_3$. The first synthesis of a 4-keto-2-alkenoic acid was reported by Koenigs and Wagstaffe (559) in 1883. These authors prepared an acid melting at $126^\circ C$. which they believed to be 4-keto-2-pentenoic. Breusch and Keskin (560) synthesized a series of 4-keto-2-alkenoic acids from C_6 to C_{10} and Keskin (561) extended the series from C_{11} to C_{15} . All of the acids melted below the temperature of that reported by Koenigs and Wagstaffe for 4-keto-2-pentenoic acid.

The synthesis of Breusch and Keskin consisted of condensing a methyl ketone, RCH_2COCH_3 , with chloral, $HCOCCl_3$, to give a 1-trichloro-2-hydroxy-4-ketoparaffin which was then hydrolyzed to yield the desired 4-ketoalkenoic acid. The reaction may be illustrated as follows:



TABLE 23
Ketoalkenoic Acids

Systematic name	Molecular formula	Structural formula, R-COOH	For- mula weight	M.p., ° C.	Derivative, M.p., ° C.
4-Keto-2-pentenoic	C ₅ H ₆ O ₃	CH ₃ COCH:CH—	114.10	126 (?)	
4-Keto-2-hexenoic	C ₆ H ₈ O ₃	CH ₃ CH ₂ COCH:CH—	128.12	108	
4-Keto-2-heptenoic	C ₇ H ₁₀ O ₃	CH ₃ (CH ₂) ₂ COCH:CH—	142.15	111	
4-Keto-2-octenoic	C ₈ H ₁₂ O ₃	CH ₃ (CH ₂) ₃ COCH:CH—	156.18	105	
4-Keto-2-nonoic	C ₉ H ₁₄ O ₃	CH ₃ (CH ₂) ₄ COCH:CH—	170.20	117	
4-Keto-2-decenoic	C ₁₀ H ₁₆ O ₃	CH ₃ (CH ₂) ₅ COCH:CH—	184.23	110	Semicarbazone 119
4-Keto-2-hendecenoic	C ₁₁ H ₁₈ O ₃	CH ₃ (CH ₂) ₆ COCH:CH—	198.25	115	S-Benzylthiuronium salt 153.5
4-Keto-2-dodecenoic	C ₁₂ H ₂₀ O ₃	CH ₃ (CH ₂) ₇ COCH:CH—	212.28	110	S-Benzylthiuronium salt 157
4-Keto-2-tridecenoic	C ₁₃ H ₂₂ O ₃	CH ₃ (CH ₂) ₈ COCH:CH—	226.31	116	S-Benzylthiuronium salt 154
4-Keto-2-tetradecenoic	C ₁₄ H ₂₄ O ₃	CH ₃ (CH ₂) ₉ COCH:CH—	240.33	113	
4-Keto-13-tetradecenoic	C ₁₄ H ₂₄ O ₃	CH ₂ :CH(CH ₂) ₈ CO(CH ₂) ₂ —	240.33	79.5	
4-Keto-2-pentadecenoic	C ₁₅ H ₂₆ O ₃	CH ₃ (CH ₂) ₁₀ COCH:CH—	254.36	116	S-Benzylthiuronium salt 138
8-Keto-16-octadecenoic	C ₁₈ H ₃₂ O ₃	CH ₃ CH:CH(CH ₂) ₇ CO(CH ₂) ₆ —	296.44	78.9	Oxime 113.5
8-Keto-17-octadecenoic	C ₁₈ H ₃₂ O ₃	CH ₂ :CH(CH ₂) ₈ CO(CH ₂) ₆ —	296.44	73	Semicarbazone 103
4-Keto-9,11,13-octadecenoic ^a	C ₁₈ H ₂₈ O ₃	CH ₃ (CH ₂) ₃ (CH:CH) ₃ (CH ₂) ₄ CO(CH ₂) ₂ —	292.40	α 74-75, β 99.5	
4-Keto- <i>trans</i> -12-heneicosenoic	C ₂₁ H ₃₈ O ₃	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₇ CO(CH ₂) ₂ —	338.51	82.5	
13-Keto-22-tricosenoic	C ₂₃ H ₄₂ O ₃	CH ₂ :CH(CH ₂) ₈ CO(CH ₂) ₁₁ —	366.57	86.7	

^a Trivial name, licanic acid.

By varying R in the parent ketone the entire series of 4-keto-2-alkenoic acids from C₆ (R = methyl) to C₁₅ (R = nonyl) was prepared.

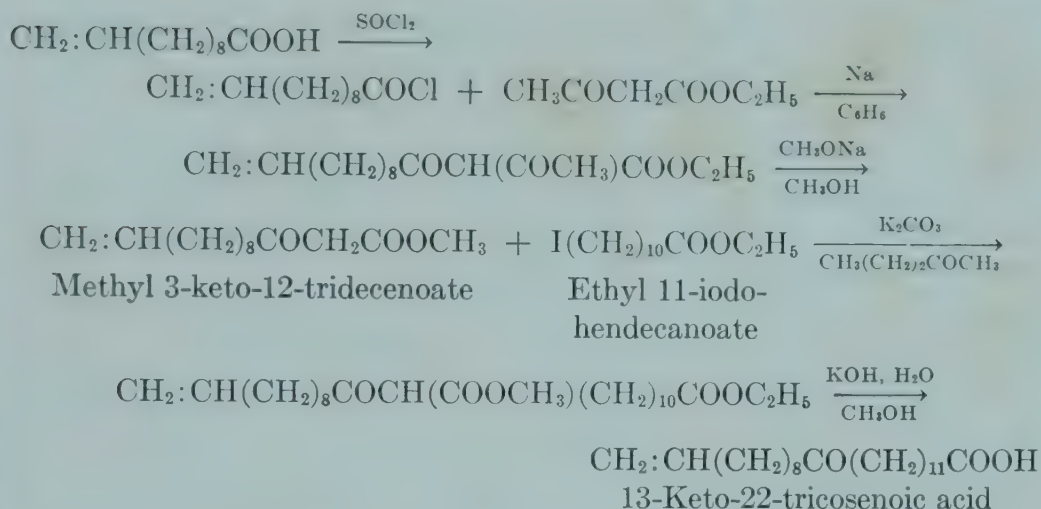
By reduction of the double bond with zinc and hydrochloric acid, the corresponding saturated 4-keto acids can be prepared, and by oxidation with cold potassium permanganate solution the corresponding 2,3-dihydroxy-4-keto acids can be prepared.

Ketotetradecenoic Acids, C₁₄H₂₄O₃. Keskin (561) synthesized 4-keto-2-tetradecenoic acid as mentioned above. Robinson (521) prepared 4-keto-13-tetradecenoic acid, CH₂:CH(CH₂)₈CO(CH₂)₂COOH, (m.p. 79.5° C.) by a variation of the Robinson-Robinson (522) keto-acid synthesis. The keto acid was used as an intermediate in the preparation of 4-hydroxy-13-tetradecenoic acid described earlier in this chapter.

Keto-octadecenoic Acids, C₁₈H₃₂O₃. Two keto-octadecenoic acids, 8-keto-16-octadecenoic and 8-keto-17-octadecenoic, have been described by Kapp and Knoll (562). Both were prepared by the acetoacetic ester synthesis using 9-hendecenoyl and 10-hendecenoyl chloride, respectively. In the first instance 9-hendecenoyl chloride was condensed with sodiodiethylacetyl suberate to yield α-acetyl-α-9-hendecenoyldiethyl suberate which was stepwise hydrolyzed by the procedure of Robinson (521,522) to give 8-keto-16-octadecenoic acid, CH₃CH:CH(CH₂)₇CO(CH₂)₆COOH, (m.p. 78.4–78.9° C.). The isomeric 8-keto-17-octadecenoic acid, CH₂:CH(CH₂)₈CO(CH₂)₆COOH (m.p. 72.2–73° C.) was prepared in the same manner from 10-hendecenoyl chloride. Both were reduced to the corresponding 16- and 17-hendecenoic acids by the Wolff-Kishner (sodium ethoxide-hydrazine hydrochloride) method.

Ketoheneicosenoic Acids, C₂₁H₃₈O₃. 4-Keto-trans-12-heneicosenoic acid, CH₃(CH₂)₇CH:CH(CH₂)₇CO(CH₂)₂COOH, (m.p. 82.5° C.), was prepared by Robinson (521) who condensed elaidoyl chloride with ethyl sodioacetosuccinate followed by stepwise hydrolysis of the condensation product.

Ketotricosenoic Acids, C₂₃H₄₂O₃. 13-Keto-22-tricosenoic acid, CH₂:CH(CH₂)₈CO(CH₂)₁₁COOH, was synthesized by Stenhagen (563) starting with 10-hendecenoic acid. The acid was converted to the chloride by treatment with thionyl chloride and the chloride condensed with ethyl acetoacetic acid in the presence of sodium and benzene. The condensation product was hydrolyzed in methanol which gave methyl 3-keto-12-tridecenoate (m.p. 9° C.). This ester was alkylated with ethyl 11-iodohendecanoate and the product subjected to hydrolysis and ketone cleavage which yielded 13-keto-22-tricosenoic acid (m.p. 86.5–86.7° C.). The various steps of the synthesis may be represented as follows:



Keto-octadecatrienoic (Licanic) Acids, $\text{C}_{18}\text{H}_{28}\text{O}_3$. Licanic or 4-keto-9,11,13-octadecatrienoic acid, $\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})_3(\text{CH}_2)_4\text{CO}(\text{CH}_2)_2\text{COOH}$, is the only unsaturated keto acid which has been isolated from a natural fat. In addition to the ketonic oxygen attached at the fourth carbon atom, the acid contains three conjugated double bonds in the same position as in eleostearic acid, hence it is sometimes referred to as keto-eleostearic acid.

Licanic acid was first isolated by Wilborn (564) in 1931 from the seed fat of *Licania rigida*, a tree native to the semiarid areas of northeast Brazil. The source of the oil examined by Wilborn had been erroneously attributed to *Couepia grandiflora* and he therefore named the new acid couepic acid from its supposed origin. In 1931, van Loon and Steger (565) also reported an examination of couepic acid (m.p. $74\text{--}75^\circ\text{C}$.) and concluded it was a conjugated trienoic acid isomeric with α - and β -eleostearic acid. Kappelmeier (566) reported that β -couepic acid contained a ketone group since it gave a semicarbazone melting at $134\text{--}137^\circ\text{C}$.

Brown and Farmer (567) investigated authentic samples of Brazilian oiticica oil and oil extracted by them from oiticica kernels definitely identified as originating from *Licania rigida*. From both sources they isolated in 25 to 33% yield an acid melting at $74\text{--}75^\circ\text{C}$. which they termed licanic acid. Oxidation of the acid with dilute potassium permanganate at 0°C . gave valeric, ketoazelaic, and oxalic acids. The acid absorbed three moles of hydrogen with the formation of 4-ketostearic acid (m.p. 96.5°C .) identical with synthetic 4-ketostearic acid. On the basis of these observations they assigned licanic (couepic) acid the structure 4-keto-9,11,13-octadecatrienoic acid and concluded that the higher melting (m.p.

96.5° C.) or β -form, which they called isolicanic acid, possessed a *trans*-configuration. In a second communication they reported a new melting point (99.5° C.) for β -licanic acid and melting points of 110–111° and 138° C., for the respective semicarbazones of α - and β -licanic acids.

The structure assigned licanic acid by Brown and Farmer was verified by Morrell and Davis (568) who also concluded that α - and β -licanic acids had geometric configurations identical to those of α - and β -eleostearic acids, namely, *cis*-9,*trans*-11,*trans*-13 and *trans*-9,*cis*-11,*cis*-13, respectively, but Paschke *et al.* (569) later concluded that the β -form possessed an all *trans*-configuration.

In addition to its presence in the seed fat of *Licania rigida*, licanic acid has been found in other species of this genus, namely, *L. arborea* (caca-huananche) (570) of Mexico, *L. crassifolia* (571) of the East Indies, and *L. venosa* (572) of British Guiana. The acid comprises 50–80% of the total fatty acids of the seed fats of these species (570–573).

Licanic acid, usually accompanied by eleostearic acid, is found to the extent of 35–70% of the total fatty acids of the seed fats of several species of *Parinarium*, especially *P. corymbosum* (taritih) (574) and *P. glaberrimum* (575) of the East Indies, *P. laurinum* (makita) (576) of the Fiji and other islands of the Pacific, *P. macrophyllum* (neou) (577) and *P. sherbroense* (po-yoak) (578) of Sierre Leone and West Africa.

α -Licanic acid isomerizes to the higher melting β -licanic or 4-keto-*trans*-9,*trans*-11,*trans*-13-octadecatrienoic acid by the action of light and more readily in the presence of a trace of iodine or sulfur. Under ordinary conditions of bromination and thiocanogenation both forms of the acid absorb two moles of bromine and one mole of thiocyanogen. They yield maleic anhydride adducts melting at 79° and 97° C., respectively. Both acids readily undergo heat-polymerization and are therefore used in the form of their glyceride oils in the protective- and decorative-coating industry for the manufacture of alkali- and water-resistant films in the same manner as tung oil and its acids.

(k) Epoxyalkenoic Acids

Epoxy fatty acids, like the keto acids, rarely occur in natural fats and only one authentic natural acid of this type is known. A number of epoxy acids have been prepared artificially, principally by oxidation of natural unsaturated fatty acids. Products of this type, for example, 9,10-epoxy-stearic acid prepared by oxidation of oleic acid, are always saturated, whereas the one known natural epoxy acid, vernolic, is unsaturated. The artificially prepared epoxy acids are discussed in Chapter XIII.

Epoxyoctadecenoic (Vernolic) Acid, $C_{18}H_{32}O_3$. Vernolic or 12,13-epoxy-9-octadecenoic acid was first isolated in 1939 by Vidyarthi (579) from the seed fat of *Veronia anthelmintica* in which it forms more than 70% of the total fatty acids.

Vidyarthi believed the product was a hydroxy acid isomeric with ricinoleic and he assigned it a structure corresponding to 11-hydroxy-9-octadecenoic. It was later shown by Gunstone (580) to be an epoxy acid having the structure



The acid is liquid at room temperature and is optically active, $[\alpha]_D -8^\circ$. When the epoxide ring is opened it yields 12,13-dihydroxy-*cis*-9-octadecenoic acid melting at $53-54^\circ \text{C}$. which on hydrogenation is converted to 12-13-dihydroxystearic acid melting at $95-96^\circ \text{C}$. Isomerization of the 12,13-dihydroxy-*cis*-9-octadecenoic acid yields the corresponding *trans*-acid melting at $67.5-69.5^\circ \text{C}$.

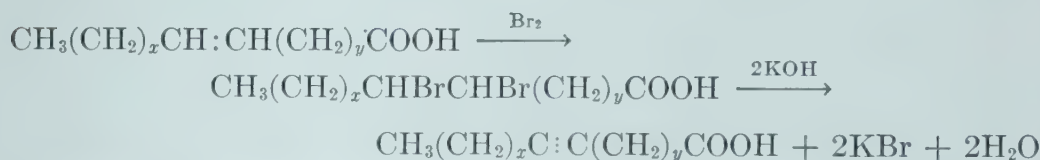
5. Alkynoic (Acetylenic) Acids

The known naturally occurring alkynoic (acetylenic, ethynoic) acids comprise a group of acids having hydrocarbon chains containing one or more triple bonds, double and triple bonds, double and triple bonds and a hydroxyl group. In addition to several natural acids an extensive number of related acids have been prepared synthetically, especially for use as intermediates in the synthesis of keto acids. For a more extensive review of the natural and synthetic acids the reader should consult Meade (580a) for the former and Raphael (580b) for the latter.

Alkynoic acids, when treated with sulfuric and other hydrolyzing agents, add a molecule of water at the triple bond with the formation of a mono-keto acid; oxidation under appropriate conditions results in the formation of a diketo acid at the triple bond. The alkynoic acids are less readily oxidized than the corresponding alkenoic acids, and unlike the alkenoic (olefinic) acids and especially alkadienoic (diolefinic) acids, they are not oxidized by air.

Alkynoic acids, add one mole of halogen readily and a second mole with difficulty. The esters and salts of α,β -alkynoic acids add one or two moles of sodium bisulfite, ammonia, primary amine, or secondary amine. The hydrogen adds to the α -carbon atom and the rest of the molecule to the β -carbon. This is a type of 1:4-addition initiated at the carboxyl group.

Several methods have been used to prepare alkynoic acids, some of which are of limited applicability and others are rather general, especially for preparing lower members of the series. One of the most generally used methods consists in removing hydrogen halides (dehydrohalogenation) from diiodo or dibromo acids by reaction with alcoholic potassium hydroxide. Diiodo and dibromo acids can be prepared easily from alkenoic acids; consequently, the method of dehydrohalogenation has been used extensively for the preparation of alkynoic acids. Other dehydrohalogenation reagents, such as sodamide, sodium and liquid ammonia, and potassium xanthate, have been used in the place of alcoholic potassium hydroxide. This method is especially useful for preparing alkynoic acids with a triple bond remote from the carboxyl group because of the availability of natural or synthetic alkenoic acids which can be brominated with ease and subsequently dehydrobrominated as indicated in the following reactions:



2-Alkynoic acids can be prepared by the reaction of a metallic acetylide of the general formula $\text{RC}:\text{CNa}$ and carbon dioxide or chlorocarbonic ester in the presence of anhydrous diethyl ether. When chlorocarbonic ester is used the ester of the alkynoic acid is obtained. The metal acetylide method yields an acid having one more carbon atom than the acetylide employed as indicated in the following equations.



A similar method (581) involves the condensation of an alkylacetylene with an α,ω -iodochloroparaffin in the presence of sodamide, converting the chlorocondensation product to the nitrile and hydrolyzing the latter to the corresponding acid as illustrated in the following equations.



The straight-chain monoalkynoic acids are sometimes referred to as propiolic or propynoic acids, a term derived from the lowest member of

the series. The general formula for the straight-chain alkynoic acids is $C_nH_{2n-3}COOH$ or $C_nH_{2n-4}O_2$.

Data with reference to synthetic and natural alkynoic (acetylenic) acids have been assembled in Tables 24 and 25.

TABLE 24
Alkynoic (Acetylenic) Acids

Systematic name	Common or other name	Formula	M.p., ° C.	B.p., ° C./mm.	Derivatives M.p., ° C.
Propynoic	Propiolic	$C_3H_2O_2$	9	83/50	Ethyl ester, b.p. 119.5
2-Butynoic	Tetrollic	$C_4H_4O_2$	76.5	203	
2-Pentynoic	Ethylpropiolic	$C_5H_6O_2$	50		
4-Pentynoic		$C_5H_6O_2$	57	203/766	
2-Hexynoic		$C_6H_8O_2$	27 ^a	125/20	
2-Heptynoic	2-Enanthynoic	$C_7H_{10}O_2$	< -20 ^a	135/20	
6-Heptynoic	6-Enanthynoic	$C_7H_{10}O_2$		93/1	<i>p</i> -Toluidide, 84-85
2-Octynoic		$C_8H_{12}O_2$	2 ^a	148/19	Methyl ester, b.p. 107/20
7-Octynoic		$C_8H_{12}O_2$		97/1	Anilide, 59-60
2-Nonynoic		$C_9H_{14}O_2$	8 ^a	159/18	
2-Decynoic		$C_{10}H_{16}O_2$	6-10	166/20	
2-Hendecynoic	2-Undecynoic	$C_{11}H_{18}O_2$	30 ^a	Dec.	
6-Hendecynoic	6-Undecynoic	$C_{11}H_{18}O_2$	0	129/1	<i>p</i> -Nitroanilide, 78-79
9-Hendecynoic	9-Undecynoic	$C_{11}H_{18}O_2$	59.5 ^a	177/15	
10-Hendecynoic	10-Undecynoic	$C_{11}H_{18}O_2$	42.8 ^a	175/15	
6-Dodecynoic		$C_{12}H_{20}O_2$	< -20	113/1	
7-Dodecynoic		$C_{12}H_{20}O_2$	18.5	142/1	Anilide, 40-41
8-Tridecynoic		$C_{13}H_{22}O_2$	8	150/1	Anilide, 41-41.5
9-Tridecynoic		$C_{13}H_{22}O_2$	23	152/1	Anilide, 51.5-52
7-Tetradecynoic		$C_{14}H_{24}O_2$	29.5		Anilide, 47.5-48
7-Hexadecynoic		$C_{16}H_{28}O_2$	47	240/15	
2-Heptadecynoic		$C_{17}H_{30}O_2$	44		
5-Octadecynoic	5-Stearolic	$C_{18}H_{32}O_2$	52.5		
6-Octadecynoic	Tariric, 6-stearolic	$C_{18}H_{32}O_2$	51.5		
7-Octadecynoic	7-Stearolic	$C_{18}H_{32}O_2$	49.3		
8-Octadecynoic	8-Stearolic	$C_{18}H_{32}O_2$	47.5		
9-Octadecynoic	9-Stearolic	$C_{18}H_{32}O_2$	48	260	
10-Octadecynoic	10-Stearolic	$C_{18}H_{32}O_2$	47		
11-Octadecynoic	11-Stearolic	$C_{18}H_{32}O_2$	46		
13-Docosynoic	Behenolic	$C_{22}H_{40}O_2$	57.5		
21-Tricosynoic		$C_{23}H_{44}O_2$	84.6		Amide 114.3-114.5
22-Tricosynoic		$C_{23}H_{44}O_2$	90		Amide 107.2-107.6

^a Freezing point.

TABLE 25
Alkynoic (Acetylenic) Acids from Natural Sources

Systematic name	Common name	Molecular formula	Formula weight	M.p., ° C.	Neutralization value	Source
6-Octadecynoic	Tariric	$C_{18}H_{32}O_2$	280.44	50.5-51.5	200.06	<i>Picramnia</i> sp.
<i>trans</i> -11-Octadecene-9-ynoic	Ximenynic (santalbic)	$C_{18}H_{30}O_2$	278.42	40-41	201.51	<i>Ximenia</i> and <i>Santalum</i> sp.
8-Hydroxy- <i>trans</i> -11-octadecene-9-ynoic	Ximenynolic	$C_{18}H_{36}O_3$	290.39		193.20	<i>Ximenia caffra</i> oil
17-Octadecene-9,11-diynoic	Isanic (erythrogenic)	$C_{18}H_{36}O_2$	274.39	39-40	204.47	Isano (boleko) seed oil
<i>cis</i> - <i>g</i> -Octadecene- <i>g</i> -ynoic	Bolekic	$C_{18}H_{36}O_2$	274.39	17	204.47	Isano (boleko) oil
8-Hydroxy-17-octadecene-9,11-diynoic	Isanolic	$C_{18}H_{36}O_3$	290.39		193.20	Isano (boleko) oil

Propynoic Acid, $C_3H_2O_2$. Propynoic (propiolic, propargylic, acetylene carboxylic) acid, $CH:CCOOH$, can be prepared by dehydrobromination of dibromopropionic acid with alcoholic potassium hydroxide. The reaction is ordinarily represented as occurring in two steps as follows:



It may also be prepared from monosodium acetylide or mono-Grignard derivatively by reaction with carbon dioxide in anhydrous diethyl ether.



Propynoic acid is best prepared from maleic acid which can be brominated and the bromo acid dehydrobrominated, followed by decarboxylation by heating with the potassium salt of acetylene dicarboxylic acid.

The acid is a pungent liquid (m.p. $9^\circ C.$) which decomposes when heated to a temperature of about $144^\circ C.$, but which can be distilled at reduced pressure (b.p. $83^\circ C./50\text{ mm.}$). Its density is 1.139_{15}^{15} . Propynoic acid is soluble in water, ethanol, and diethyl ether. The hydrogen of the acetylenic radical as well as that of the carboxyl group can be replaced by a metal. The triple bond can be reduced readily to form first acrylic and then propionic acid. Propynoic acid undergoes polymerization in sunlight, forming benzene-1,3,5-tricarboxylic (trimesic) acid in small yield.

Butynoic (Tetrolic) Acid, $C_4H_4O_2$. Tetrolic (methylpropiolic, 2-buty-noic) acid, $CH_3C:CCOOH$, can be prepared from crotonic acid, $CH_3CH:CHCOOH$, by bromination and dehydrohalogenation, or from allylene (methylacetylene), $CH_3C:CH$, via its sodium or Grignard derivative. Tetrolic acid melts at $76.5^\circ C.$, boils at $203^\circ C.$, is very soluble in water and diethyl ether. It also dissolves to a limited extent in carbon disulfide, 8.33g./100 ml.

Hydrogenation of tetrolic acid in the presence of palladium catalyst at $20^\circ C.$ yields *cis*-isocrotonic acid. Its behavior with other reagents is similar to that described for propynoic acid.

Pentynoic acids, $C_5H_6O_2$. Three pentynoic acids, namely, 2-, 3-, and 4-pentynoic, are known. 2-Pentynoic (ethylpropiolic), $CH_3(CH_2C:CCOOH)$, was prepared by Jocitsch and Faworsky (582) in 1897 by the action of carbon dioxide on sodium ethylacetylide, $C_2H_5C:CNa$, in dry diethyl ether, and by Dupont (583) by the action of carbon dioxide on 1-butylnmagnesium bromide. The acid melts at $50^\circ C.$, is very soluble in water, and gives the normal reactions for 2-alkynoic acids.

4-Pentynoic acid, $CH:CCCH_2CH_2COOH$, was first prepared by Perkin

and Simonsen (584) by pyrolysis of 2-carboxy-4-pentynoic (4-pentyn-2-dioic) acid, $\text{CH}:\text{CCH}_2\text{CH}(\text{COOH})_2$, which had been prepared previously by treating ethyl 2-carbethoxy-4-bromo-4-pentenoate with alcoholic potassium hydroxide.

Gardner and Perkin (585) prepared the acid by reacting 1,2,3-tribromopropane (tribromohydrin) with ethyl acetate in the presence of sodium and ethanol which gave ethyl 2-acetyl-4-bromo-4-pentenoate. Reaction of the ester with alcoholic potassium hydroxide gave 4-pentynoic acid. 4-Pentynoic acid has also been prepared by reacting tribromohydrin with sodiomalonic ester, and by reacting 2-bromoallyl bromide with malonic ester.

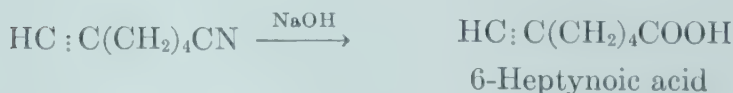
4-Pentynoic acid freezes at 57°C ., boils at $203^\circ \text{C}/766 \text{ mm.}$, is soluble in water, ethanol, diethyl ether, and other organic solvents.

Hexynoic Acids, $\text{C}_6\text{H}_8\text{O}_2$. A series of 2-alkynoic acids from $\text{C}_6\text{H}_8\text{O}_2$ to $\text{C}_{10}\text{H}_{12}\text{O}_2$ was prepared by Faworsky (586) and also by Moureu and Delange (587) by reaction of carbon dioxide on alkyl sodium acetylides, $\text{RC}:\text{CNa}$., containing one less carbon atom than the desired acid. 2-Hexynoic acid, $\text{CH}_3(\text{CH}_2)_2\text{C}:\text{CCOOH}$, was prepared in this manner from sodium propylacetylide, $\text{CH}_3(\text{CH}_2)_2\text{C}:\text{CNa}$. 2-Hexynoic acid and its higher homologs are sparingly soluble in water, but are readily soluble in ethanol, diethyl ether, and other organic solvents.

Heptynoic (Enanthynoic) Acids, $\text{C}_7\text{H}_{10}\text{O}_2$. Two positionally isomeric heptynoic acids have been prepared, namely, 2-heptynoic, $\text{CH}_3(\text{CH}_2)_2\text{C}:\text{CCOOH}$, and 6-heptynoic, $\text{CH}:\text{C}(\text{CH}_2)_4\text{COOH}$. The 2-isomer was prepared as mentioned under hexynoic acid with sodium butylacetylide, $\text{CH}_3(\text{CH}_2)_3\text{C}:\text{CNa}$, as the parent material.

Taylor and Strong (588) prepared a series of 6- and 7-alkynoic acids from heptynoic to tetradeconoic as intermediates in the synthesis of the corresponding alkenoic acids. They employed the general method of condensing an alkylacetylene with the appropriate iodochloroparaffin.

6-Heptynoic acid was prepared by condensing sodium acetylide with α,ω -iodochlorobutane and converting the chlorohydrocarbon to the nitrile, followed by hydrolysis of the nitrile to the desired acid.



Octynoic Acids, $C_8H_{12}O_2$. Two octynoic acids, namely, 2-octynoic, $CH_3(CH_2)_4C:CCOOH$, and 7-octynoic, $CH:C(CH_2)_5COOH$, have been synthesized. The former was prepared (582,583) from carbon dioxide and sodium propylacetylide as previously described. 2-Octynoic acid is reported to have a density of $0.9623_4^{12.6}$ and a refractive index of $1.46335_D^{12.6}$.

7-Octynoic acid was prepared by Newman and Wotiz (589) and by Taylor and Strong (588). The latter authors condensed sodium acetylide and 1-chloro-4-iodobutane and converted the resulting chlorohydrocarbon to the nitrile followed by hydrolysis of the nitrile to 7-octynoic acid.

Newman and Wotiz reported the following characteristics for 7-octynoic acid: m.p. $20^\circ C.$, b.p. $123^\circ C./2\text{ mm.}$, refractive index 1.4502_D^{25} . The preparation of Taylor and Strong boiled at $97^\circ C./1\text{ mm.}$ and had a refractive index of 1.4506_D^{25} .

Nonynoic Acids, $C_9H_{14}O_2$. 2-Nonynoic acid, $CH_3(CH_2)_5C:CCOOH$, was prepared (586,587) by reacting carbon dioxide in dry diethyl ether with sodium hexyacetylide, $CH_3(CH_2)_5C:CNa$. The acid is a liquid at room temperature; density $0.9525_4^{12.5}$; refractive index $1.46429_D^{12.5}$; is insoluble in water; soluble in ethanol, diethyl ether, and other organic solvents.

Decynoic Acids, $C_{10}H_{16}O_2$. 2-Decynoic acid, $CH_3(CH_2)_6C:CHCOOH$, was prepared (586,587) in the manner previously described for 2-alkynoic acids, using in this case sodium heptylacetylide as the parent material. The acid is a liquid at ordinary temperatures and has a density of 0.9408_4^{19} . Its solubility properties are similar to those described for 2-nonynoic acid.

Hendecynoic (Undecynoic) Acids, $C_{11}H_{18}O_2$. Nine position isomers of hendecynoic acid are theoretically possible. None has been observed as a constituent of natural fats but several of them have been synthesized.

2-Hendecynoic acid, $CH_3(CH_2)_7C:CCOOH$, was prepared by Moureu and Delange (587) by the action of carbon dioxide on sodium octylacetylide in dry diethyl ether. The acid melts at $30^\circ C.$ and decomposes into 1-decyne and carbon dioxide on distillation at atmospheric pressure.

6-Hendecynoic acid, $CH_3(CH_2)_3C:C(CH_2)_4COOH$, was prepared by Taylor and Strong (588) by condensing sodium propylacetylide with 1-chloro-4-iodobutane, followed by conversion of the chlorohydrocarbon to the nitrile and hydrolyzing the nitrile to the acid. The acid melts at -1° to $+1^\circ C.$, boils at $128-130^\circ C./1\text{ mm.}$, and has refractive index of 1.4566_D^{25} . A previous preparation by Ahmad and Strong (590) had the same refractive index and boiled at $124-125^\circ C.$ 0.17 mm.

9-Hendecynoic acid, $\text{CH}_3\text{C}:\text{C}(\text{CH}_2)_7\text{COOH}$, has been prepared by dehydrobromination of 10,11-dibromohendecanoic acid with concentrated aqueous potassium hydroxide (591) and also with alcoholic potassium hydroxide (592). Krafft (592) reported that dehydrobromination of 10,11-dibromohendecanoic acid with either reagent produced 9-hendecynoic acid, and also that treatment of 10-hendecynoic acid with either reagent resulted in the migration of the triple bond from the 10- to the 9-position. 9-Hendecynoic acid is a solid (m.p. 59.5°C .) which is only slightly soluble in water but readily soluble in ethanol, diethyl ether, and carbon disulfide.

10-Hendecynoic acid, $\text{CH}:\text{C}(\text{CH}_2)_8\text{COOH}$, has been prepared by several different methods. It was first obtained by Krafft (592) by dehydrobromination of 10,11-dibromohendecanoic acid with potassium carbonate in ethanol solution. He reported that the acid melted at $42.7\text{--}42.9^\circ\text{C}$. and boiled at $175^\circ\text{C}/15\text{ mm}$. Khan (593) obtained 10-hendecynoic acid in 40–42% yield by dehydrobromination of dibromohendecanoic acid with sodamide in liquid ammonia.

Dodecynoic Acids, $\text{C}_{12}\text{H}_{20}\text{O}_2$. Taylor and Strong (588) prepared 6-dodecynoic acid, $\text{CH}_3(\text{CH}_2)_4\text{C}:\text{C}(\text{CH}_2)_4\text{COOH}$, and 7-dodecynoic acid, $\text{CH}_3(\text{CH}_2)_3\text{C}:\text{C}(\text{CH}_2)_5\text{COOH}$, by condensing the appropriate sodium alkylacetylides and iodochloroalkanes, converting the chloroparaffins to the nitriles, and hydrolyzing the nitriles to the desired alkynoic acids in the manner previously described. Both acids are liquids at ambient temperature, having refractive indices of 1.4462_D^{25} and 1.4568_D^{25} , respectively.

Tridecynoic Acids, $\text{C}_{13}\text{H}_{22}\text{O}_2$. Two tridecynoic acids, namely, 6-tridecynoic, $\text{CH}_3(\text{CH}_2)_5\text{C}:\text{C}(\text{CH}_2)_4\text{COOH}$, and 7-tridecynoic, $\text{CH}_3(\text{CH}_2)_4\text{C}:\text{C}(\text{CH}_2)_5\text{COOH}$, were prepared by Taylor and Strong (588) by condensing the appropriate sodium alkylacetylides and iodochloroalkanes, converting the chloroparaffins to the nitriles, and hydrolyzing the nitriles to the desired acids. 6-Tridecynoic acid is a liquid at room temperature and 7-tridecynoic acid is a low melting solid (m.p. $22\text{--}24^\circ\text{C}$.). Refractive indices of the respective acids are 1.4574_D^{25} and 1.4653_D^{25} .

Tetradecynoic Acids, $\text{C}_{14}\text{H}_{24}\text{O}_2$. 7-Tetradecynoic acid, $\text{CH}_3(\text{CH}_2)_5\text{C}:\text{C}(\text{CH}_2)_5\text{COOH}$, was prepared by Taylor and Strong (588) by condensing sodium hexylacetylide with 1-chloro-5-iodopentane, converting the chloroparaffin condensation product to the nitrile, and hydrolyzing the nitrile to the desired acid. 7-Tetradecynoic acid is a low-melting solid (m.p. $29.5\text{--}30^\circ\text{C}$.) and has a refractive index of 1.4571_D^{32} .

Hexadecynoic Acids, $\text{C}_{16}\text{H}_{28}\text{O}_2$. 7-Hexadecynoic acid, $\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_2)_5\text{COOH}$, was prepared by Bodenstein (594) by dehydrobromina-

tion of 7,8-dibromopalmitic acid with alcoholic potassium hydroxide. The acid is a crystalline solid, insoluble in water, and readily soluble in ethanol and diethyl ether.

Heptadecynoic Acids, $C_{17}H_{30}O_2$. 2-Heptadecynoic acid, $CH_3(CH_2)_{13}C:CCOOH$, was prepared by Krafft and Heinzmann (595) by the action of carbon dioxide on sodium tetradecylacetylide in dry diethyl ether. The acid is a crystalline solid; is insoluble in water, but soluble in ethanol and diethyl ether. On distillation at atmospheric pressure it decomposes into 1-hexadecyne and carbon dioxide.

Octadecynoic Acids, $C_{18}H_{32}O_2$. The octadecynoic acids are the best-known alkynoic acids and constitute the most complete series of position isomers of this class of compounds. Of the sixteen theoretically possible position isomers, six have been synthesized and a seventh isomer (tariric) has been found as a constituent of natural fats. The octadecynoic acids are often referred to as stearolic acids because the 9-isomer (stearolic) was first prepared from dibromostearic acid and hence was considered to be acetylenic stearic acid.

5-Octadecynoic acid, $CH_3(CH_2)_{11}C:C(CH_2)_3COOH$, was first prepared by Posternak (596) from naturally occurring tariric (6-octadecynoic) acid by addition of two molecular equivalents of hydrogen iodide followed by dehydroiodination of the addition product with alcoholic potassium hydroxide. Dehydrohalogenation resulted in a mixture of difficultly separable isomeric octadecynoic acids one of which was tariric. The latter acid was removed from the mixture and the residue again treated successively with hydrogen iodide and alcoholic potassium hydroxide which gave two new acids, namely, 5-octadecynoic and 7-octadecynoic.

After separation and purification, 5-octadecynoic acid was obtained as a crystalline solid melting at $52.5^\circ C$. and soluble in the usual organic solvents for alkynoic acids. On mild oxidation 5-octadecynoic acid yields 5,6-diketostearic acid (m.p. $94^\circ C$). 5,6-Diodooctadecenoic, *trans*-5-octadecenoic, and 5,6-dihydroxyoctadecenoic acids were prepared from the alkynoic acid.

6-Octadecynoic (tariric) acid, $CH_3(CH_2)_{10}C:C(CH_2)_4COOH$, was first noted by Arnaud (597) in 1892 as a constituent of the seed oil of tariric (bitterbush), *Picramnia Sow.* family Simarubaceae. Nearly twenty years later it was reported by Grimme to be present in the seed oils of other species of this genus, namely, *P. Cambaita* (598a), *P. Carpinterae* (598a), and *P. Lindeniana* (598b). Steger and van Loon (599) reported that the acid comprised 95% of the total fatty acids of the seed oil of *P. Sow.* According to Grimme (598b) it comprises only 20% of the fatty acids of the seed oil of *P. Lindeniana*.

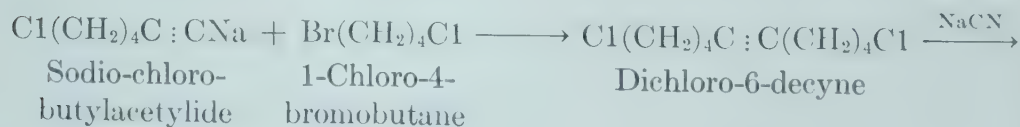
Tariric acid melts at 51.5° C. and freezes at 50.5° C. It adds one mole of iodine to form 6,7-diiodo-6-octadecenoic acid (m.p. 47–48° C.). On ozonolysis it yields lauric and adipic acids which places the triple bond between the sixth and seventh carbon atoms. On partial hydrogenation it yields petroselinic (6-octadecenoic) acid; and on complete hydrogenation it yields stearic acid. Under conditions of mild oxidation it yields 6,7-diketooctadecanoic acid, and on hydroxylation it yields 6,7-dihydroxy-octadecanoic acid (m.p. 117.5° C.). The acid forms a diiodide (m.p. 48.5° C.), a dibromide (m.p. 32° C.) and a tetrabromide (m.p. 125° C.).

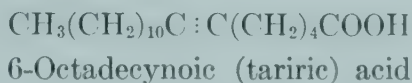
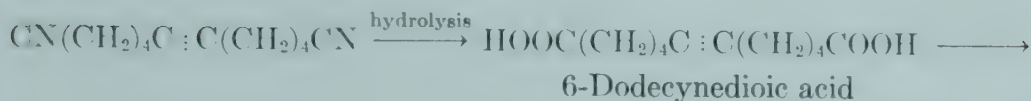
Tariric acid has been synthesized by three different methods which were reported in three successive years between 1952 and 1954. The first of these syntheses was reported by Lumb and Smith (600) who prepared the acid by reacting lithium hendecynylacetylide (tridecynyl-lithium), $\text{CH}_3(\text{CH}_2)_{10}\text{C}:\text{CLi}$, with 1-chloro-3-iodopropane, $\text{I}(\text{CH}_2)_3\text{Cl}$, to give 1-chloro-4-hexadecyne, $\text{CH}_3(\text{CH}_2)_{10}\text{C}:\text{C}(\text{CH}_2)_3\text{Cl}$. The chloroalkyne was reacted in a malonic ester syntheses to give 4-hexadecynylmalonic acid (m.p. 84° C.) which on decarboxylation at 150° C. gave 6-octadecynoic acid (m.p. 50–51° C.) identical in all respects with natural tariric acid.

Partial reduction of the sodium salt of synthetic tariric acid with hydrogen and Raney nickel catalyst gave *cis*-6-octadecenoic acid identical with natural petroselinic acid, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$, melting point at 29.2° C. Complete hydrogenation yielded stearic acid.

Khan (601) prepared 6-octadecynoic acid by bromination of natural petroselinic (6-octadecenoic) acid followed by dehydrobromination of the dibromo acid with sadimed in liquid ammonia. After purification the synthetic tariric acid melted at 48.5–48.7° C.

Baker *et al.* (602) synthesized tariric acid by the method of anodic crossed coupling of the methyl hydrogen ester of 6-dodecynedioate with *n*-octanoic acid. The synthesis required the preparation of the heretofore unknown 6-dodecynedioic acid. The latter acid was prepared by condensing sodium chlorobutylacetylide with 1-chloro-4-bromobutane, $\text{Br}(\text{CH}_2)_4\text{Cl}$, to give dichloro-6-decyne which was converted to the dinitrile and hydrolyzed to give the desired dioic acid. Electrolysis of the half-ester of this acid with *n*-octanoic acid gave tariric acid. The various steps of the synthesis may be represented as follows.



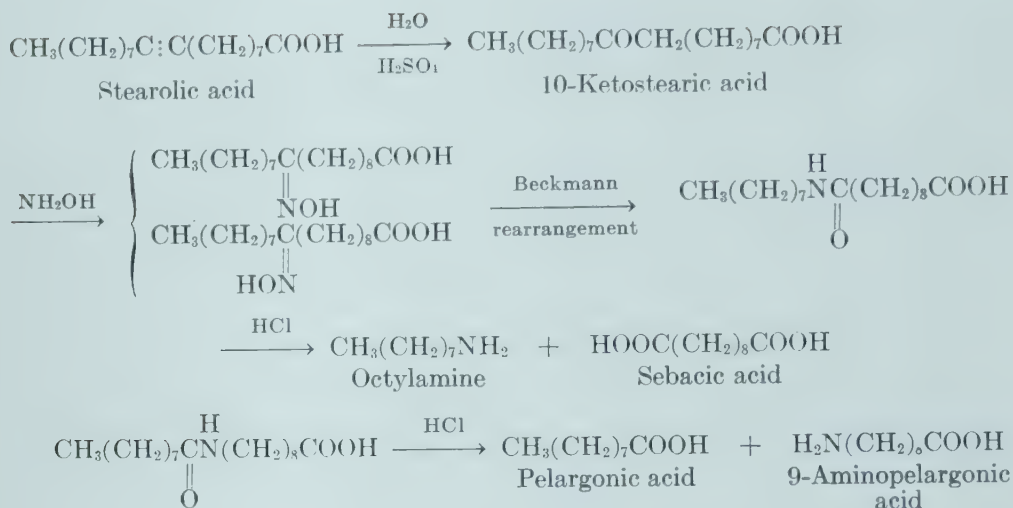


7-Octadecynoic acid, $\text{CH}_3(\text{CH}_2)_9\text{C}:\text{C}(\text{CH}_2)_5\text{COOH}$, was obtained by Posternak (596) together with the 5-isomer as has already been described. The acid melted at 49.25°C . and on oxidative fission with fuming nitric acid yielded among other products 7,8-diketostearic acid (m.p. 86.5°C .) and pimelic acid, $\text{HOOC}(\text{CH}_2)_5\text{COOH}$, melting at 103°C .

8-Octadecynoic acid, $\text{CH}_3(\text{CH}_2)_8\text{C}:\text{C}(\text{CH}_2)_6\text{COOH}$, was prepared by Arnaud and Posternak (603) by treating stearolic (9-octadecynoic) acid with two moles of hydrogen iodide which the authors claim gave a mixture 9,9-diiodo- and 10,10-diiodostearic acids. The mixed acids were dehydrohalogenated with alcoholic potassium hydroxide which gave a mixture of stearolic, 8-octadecynoic, and 10-octadecynoic acids together with an oily monoiodide. The 8- and 10-octadecynoic acids were separated from this mixture. After purification 8-octadecynoic acid was obtained as a crystalline solid melting at 47.5°C .

On oxidative fission with nitric acid the alkynoic acid gave suberic acid, $\text{HOOC}(\text{CH}_2)_6\text{COOH}$, melting at 140°C . On treatment with concentrated sulfuric acid 9-ketostearic acid (m.p. 74.5°C .) was obtained.

9-Octadecynoic (stearolic) acid, $\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_2)_7\text{COOH}$, has never been found as a constituent of natural fats but is of more than ordinary interest because of its structural similarity to oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$. The acid was first prepared by Overbeek (604) in 1866 by the action of alcoholic potassium hydroxide on 9,10-dibromostearic acid. Rigid proof of the position of the double bond in stearolic acid was first advanced by Baruch (605) in 1894. Baruch converted the acid to 10-ketostearic acid by treatment with sulfuric acid, which in turn was converted to a mixture of oximes by treatment with hydroxylamine. The mixture of oximes was subject to a Beckmann rearrangement followed by cleavage with concentrated hydrochloric acid. The cleavage products consisted of a mixture of octylamine, sebacic, pelargonic, and 9-aminopelargonic acids which would be expected if the triple bond of stearolic acid occupied the 9-position. The reactions involved may be illustrated as follows.



Stearolic acid has been prepared from a variety of starting materials and by several different routes. The original preparation by Overbeck has already been mentioned. In 1895 Behrend (606) reported its preparation from ricinoleic acid, $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$, which he converted to 9-keto-12-chlorostearic acid, $\text{CH}_3(\text{CH}_2)_5\text{CHCl}(\text{CH}_2)_2\text{CO}(\text{CH}_2)_7\text{COOH}$. According to Behrend, treatment of the chloro-ketostearic acid with zinc in a mixture of hydrochloric and acetic acids gave stearolic acid. It was also prepared by Kimura (607) by dehydrobromination of 9,10-dibromostearic acid with potassium hydroxide in 1-pentanol.

Khan *et al.* (608) prepared stearolic acid in 58–68% yield by dehydrobromination of dibromostearic acid with sodamide in liquid ammonia. This yield is claimed to be much greater than that attainable by dehydrohalogenation with alcoholic potassium hydroxide (603,604,606,607,609). Khan (608) also prepared stearolic acid by direct bromination of the crude mixture of olive oil acids followed by dehydrohalogenation with sodamide and liquid ammonia. When stearolic acid is prepared by bromination-dehydrobromination it is immaterial whether oleic or elaidic acid is used as the parent material.

Stearolic acid is a crystalline solid which melts at 48°C ., boils at 260°C ., is insoluble in water, slightly soluble in cold ethanol, and appreciably soluble in hot ethanol and diethyl ether.

Oxidation of stearolic acid with fuming nitric acid gives 9,10-diketostearic acid and other oxidation products (610). Disruptive oxidation with potassium permanganate yields pelargonic, suberic, azelaic, and caprylic acids (611). Hydrogenation of stearolic acid in the presence of

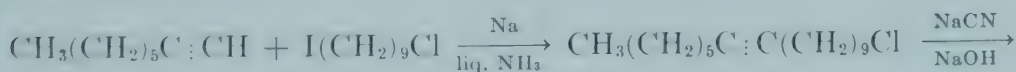
a nickel catalyst gives oleic (*cis*) acid, whereas reduction with zinc and acetic acid yields elaidic (*trans*) acid.

Hydroxyoctadecynoic Acids, $C_{18}H_{32}O_3$. Ricinstearolic acid, 12-hydroxy-9-octadecynoic, differs from ricinoleic acid only in the presence of a triple bond instead of a double bond at the 9-position. Ricinstearolic can be prepared from ricinoleic acid in the same manner that stearolic acid can be prepared from oleic acid, namely, by bromination followed by dehydrohalogenation with alcoholic potassium hydroxide. Dehydrohalogenation is somewhat more difficult to accomplish and requires a reflux period of twenty hours (612).

Ricinstearolic acid melts at 53°C . and is optically active, $[\alpha]_D + 13.67^\circ$ in acetone. Treatment with sulfuric acid converts it into 12-hydroxy-10-ketostearic acid (m.p. $84\text{--}85^\circ\text{C}$.).

10-Octadecynoic acid, $\text{CH}_3(\text{CH}_2)_6\text{C}:\text{C}(\text{CH}_2)_8\text{COOH}$, was prepared by Arnaud and Posternak (603) who obtained it, together with 8-octadecynoic acid, in the manner already described. The acid melted at 47°C . and on oxidation with nitric acid it gave sebacic acid melting at $130\text{--}130.5^\circ\text{C}$. When dissolved in concentrated sulfuric and reprecipitated with water it yielded 11-ketostearic acid melting at 73.5°C .

11-Octadecynoic acid, $\text{CH}_3(\text{CH}_2)_5\text{C}:\text{C}(\text{CH}_2)_9\text{COOH}$, was synthesized by Ahmad *et al.* (613) by the sodium acetylide method starting with *n*-hexyl bromide. The bromide was converted to 1-octyne by treatment with sodium acetylide. The alkyne was condensed with 1-chloro-9-iodononane in the presence of sodium and liquid ammonia to give 1-chloro-10-heptadecyne which was converted to the nitrile and hydrolyzed to 11-octadecynoic acid.



11-Octadecynoic acid is a crystalline solid melting at $45.5\text{--}46.5^\circ\text{C}$. On hydrogenation in ethanol solution in the presence of Raney nickel catalyst the alkynoic acid is converted into *cis*-11-octadecenoic acid (m.p. $10.5\text{--}12^\circ\text{C}$.).

Dococynoic Acids, $C_{22}H_{40}O_2$. 13-Docosynoic or behenolic acid, $\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_2)_{11}\text{COOH}$, is related to erucic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{11}\text{COOH}$, in the same manner that stearolic acid is related to oleic. The acid has not been found as a constituent of natural fats but it can be prepared from erucic acid in the same manner that stearolic acid

can be prepared from oleic, namely, by bromination followed by dehydrobromination of the dibromide (614). It can be prepared from brassidic (*trans*-erucic) acid in the same manner.

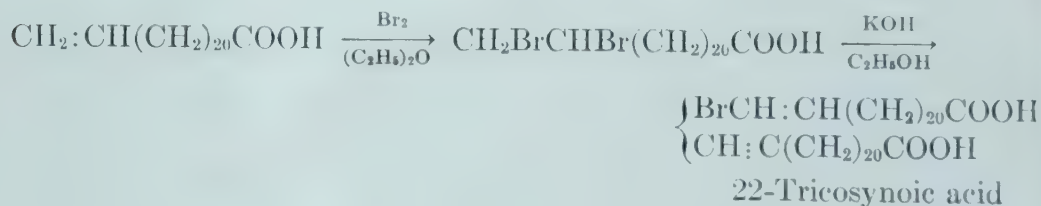
Baruch (615) proved that the structure of behenolic acid corresponded to 13-docosynoic acid by the same procedure he followed in establishing the structure of stearolic acid.

Behenolic acid melts at 57.5°C ., is insoluble in water, soluble in chloroform, and very soluble in ethanol and diethyl ether. On oxidation with nitric acid it yields 13,14-diketobehenic acid and on oxidative cleavage it yields pelargonic and tridecanedioic acid, $\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$. On mild reduction behenolic acid yields erucic (*cis*) acid and on more vigorous reduction brassidic (*trans*) acid.

Tricosynoic Acids, $\text{C}_{23}\text{H}_{42}\text{O}_2$. Two tricosynoic acids, namely, **21-tricosynoic**, $\text{CH}_3\text{C}:\text{C}(\text{CH}_2)_{19}\text{COOH}$, and **22-tricosynoic**, $\text{CH}:\text{C}(\text{CH}_2)_{20}\text{COOH}$, their methyl esters and amides were synthesized by Stenhagen (616). The two acetylenic acids were prepared from **22-tricosenoic acid**, $\text{CH}_2:\text{CH}(\text{CH}_2)_{20}\text{COOH}$, by methods analogous to those used by Krafft (592) in synthesizing the corresponding C_{11} -acids.

Tricosenoic acid was prepared in the manner already described. The alkenoic acid was brominated and the unsaturated bromo-acid dehydrobrominated with potassium hydroxide in ethanol solution which gave a mixture of ω -acetylenic acid and an unsaturated monobromo acid. As originally shown by Krafft (592) and verified by Harris and Smith (617) the bromine atom in acids of this type is attached at the terminal or ω -position.

In order to separate the desired ω -acetylenic acid, the mixed acids were converted to the corresponding methyl esters by reaction with diazomethane and the mixed esters treated with silver nitrate to convert the acetylenic acid to the insoluble silver acetylide. The soluble bromo acid was removed by extraction with ethanol and diethyl ether. The metallic acetylide was decomposed with hydrochloric acid which gave methyl **22-tricosynoate** (m.p. $62.9\text{--}63.2^{\circ}\text{C}$.) which after hydrolysis yielded the desired **22-tricosynoic acid**. The various steps in the synthesis may be represented as follows:



Tricosynoic acid melts at 89.9–90.1° C. and exhibits a long x-ray spacing 53.1 Å. The amide melts at 107.2–107.6° C. and does not exhibit polymorphism.

21-Tricosynoic acid was prepared by acetylenic rearrangement of 22-tricosynoic acid described above by the prolonged action of aqueous potassium hydroxide at 165° C. in a sealed tube. The rearranged acid was purified via the methyl ester. The methyl ester melts at 47.3–47.7° C. and is extremely soluble in low boiling petroleum naphtha. It exhibits polymorphism; a low-melting form appears on cooling the melted liquid to 43.8° C. The high-melting form exhibits a long x-ray spacing 48.8 Å., and the low-melting form a similar spacing 32.7 Å.

The regenerated acid melts at 84.5–84.7° C. and exhibits a long x-ray spacing 49.2 Å. The amide melts at 114.3–114.5° C. and remelts at 115.6–116.0° C.

Ximenynic (Santalbic) Acid, $C_{18}H_{30}O_2$. Ximenynic or *trans*-11-octadecen-9-ynoic was isolated by Lighthelm and Schwartz (618) from the seed fat of *Ximenia caffra* (family Olacaceae). Subsequently, Lighthelm *et al.* (619) reported that the acid composed 22–24% of the total fatty acids of three African species of the genus *Ximenia*, namely, *X. caffra*, *X. caffra natalensis*, and *X. americana microphylla*.

Ximenynic acid, $CH_3(CH_2)_5CH:CHC:C(CH_2)_7COOH$, differs from linoleic acid in having its unsaturation at the 9,11-position rather than at the 9,12-position. Like vaccenic acid the ethenoid linkage at the 11-position has a *trans*-configuration which was established from infrared absorption measurements by Ahlers and Lighthelm (620). The validity of the structure assigned to ximenynic acid was verified by Grigor *et al.* (621) who synthesized the acid from ricinoleic acid via 12-hydroxy-octadec-9-ynoic acid.

The acid melts at 40–41° C. and on oxidation with performic acid yields 11,12-dihydroxy-octadec-9-ynoic acid melting at 88–89° C. The methyl ester of ximenynic acid boils at 169° C./1 mm. The bromophenacyl ester melts at 53–54° C. and the amide at 105° C.

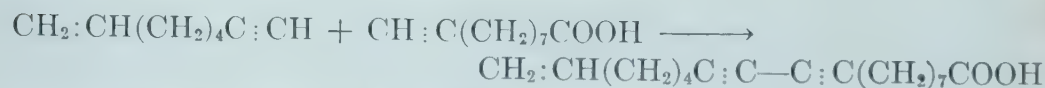
In 1938, Madhuranath and Manjunath (622) reported the presence of an unidentified acid in the seed oil of *Santalum album* (family Santalaceae). The acid, which comprised about 50% of the total fatty acids, was named santalbic acid. In 1954 Hatt and Szumer (623) reported that the acid comprised 40–43% of the total fatty acids of the seed oils of two Australian species of *Santalum*, namely, *S. acuminatum* and *S. Murrayanum*. They suggested that santalbic acid was identical with ximenynic acid. In 1956 Hatt and Schoenfeld (624) reported the examination of

the seed fats of *S. acuminatum* (sweet quandong), *S. Murrayanum* (bitter quandong), and *S. spicatum* (*Eucarya spicata*) (Australian sandalwood). All three seed fats were found to contain large proportions of santalbic acid which they termed ximenynic acid. These authors also suggested that linolenic and ximenynic acids had a common precursor in the genus *Santalum*, and that ximenynic acid was an intermediate between linolenic and oleic acids.

Almost simultaneously with the appearance of the publication of Hatt and Sumer (623), Gunstone and McGee (625) announced that santalbic acid was 11-octadecen-9-ynoic acid. Subsequently, Grigor *et al.* (626) demonstrated unequivocally that santalbic acid obtained from the seed oil of *Santalum album* was *trans*-11-octadecen-9-ynoic acid and was, therefore, identical with ximenynic acid.

Isanic (Erythrogenic) Acid, $C_{18}H_{26}O_2$. In 1896 Hébert (627) reported the isolation from isano (boleko) oil obtained from the kernels of the tree *Ongekoea Gore* Engler (family Olacaceae), indigenous to equatorial Africa, a heretofore unknown fatty acid which he called isanic acid. The same acid was reisolated in 1937 and extensively studied by Steger and van Loon (628) who reported that it contained one ethenoic (olefinic) and two ethynoic (acetylenic) linkages. In the same year Boekenoogen (629) reported the isolation of the same acid and established the fact that it contained a terminal ethenoic group and yielded ethyl hydrogen azelate, oxalic, and adipic acids on oxidative fission. Boekenoogen concluded that isanic acid was the principle fatty acid in isano oil.

In 1939 Castille (630) investigated isanic acid which he termed erythrogenic acid, and showed that its structure conformed either to 17-octadecen-9,15-diynoic or to 17-octadecen-9,11-diynoic. In 1940 Steger and van Loon (628) established the correctness of the latter structure, namely, $CH_2:CH(CH_2)_4C:C-C:C(CH_2)_7COOH$. This structure was also supported by the work of Doucet and Fauve (631) and was further verified by synthesis of the acid in 1953 by Black and Weedon (632) who prepared it by coupling 9-decynoic acid, $CH:C(CH_2)_7COOH$ with 1-octen-7-yne, $CH:C(CH_2)_4CH:CH_2$, in the presence of cuprous ammonium chloride.



With these two reactants, both self-coupling as well as cross-coupling can occur and it is to be expected that a mixture of three products would be obtained, one of which should be isanic acid. This was verified by the

isolation of isanic acid in 30% yield from the reaction mixture. The acid melted at 39° C. and exhibited other properties identical with the natural acid. The correctness of the structure assigned to isanic acid has been verified further by the work of Seher (633).

The presence of isanic and isanolic acids in isano oil imparts to it a high iodine value (143–233, depending on the method of determination) and an even higher hydrogenation-iodine value (316) which classifies it as a drying oil. However, the high degree of unsaturation results from the alkynoic linkages which, as has been mentioned earlier, do not readily absorb atmospheric oxygen; hence the oil does not dry when exposed in thin films either with or without added driers (628b). The oil polymerizes when heated to moderate temperatures and if heated rapidly above 200° C. does so with explosive violence.

The methyl ester of isanic acid boils at 175° C./1 mm. Its density is 0.9350₂₀²⁰, and refractive index 1.4939_D²⁰.

Bolekic Acid, C₁₈H₂₆O₂. In 1951 Meade (580a) reported the isolation of an acid which he designated boleikic acid. Its exact structure was not determined but on the basis of the data given below it appeared to be a conjugated mid-chain *cis*-ene-diyne octadecanoic acid. The acid absorbed 4.9 moles of hydrogen to yield stearic acid. Infrared absorption indicated *cis*-unsaturation and ultraviolet absorption typical ene-diyne configuration. The acid gave a methyl ester of density 0.9413₂₀²⁰ and refractive index 1.5179_D²⁰.

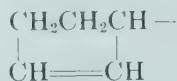
Isanolic (Hydroxyisanic) Acid, C₁₈H₂₆O₃. In 1951 Kaufmann *et al.* (634) reported the presence in isano oil of a hydroxy acid which constituted 44% of the total fatty acids. In the same year Riley (635) also reported the presence, in very considerable proportion in isano oil, of an 8-hydroxy unsaturated acid belonging to the C₁₈-series. Kaufmann *et al.*, on the basis of the similarity of the ultraviolet absorption spectra of the hydroxy acid and isanic acid, termed the former isanolic acid. They suggested that isanolic acid had a structure corresponding to 8-hydroxy-17-octadecene-9,11,-diynoic, $\text{CH}_2:\text{CH}(\text{CH}_2)_4\text{C}:\text{C}—\text{C}:\text{CCHOH}(\text{CH}_2)_6\text{COOH}$. The structure of isanolic as well as isanic acid were subsequently verified by Seher (633).

6. Alicyclic-Substituted Fatty Acids

A number of acids having a five-carbon ring attached at the terminal or *ω*-carbon atom of a saturated or unsaturated aliphatic chain has been found in natural fats. These acids are confined principally to the group

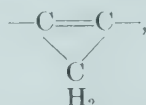
of oils known collectively as chaulmoogra oils which have been used in various forms for the treatment of human leprosy. At least seven such acids have been isolated from natural sources and a large number of related acids have been prepared synthetically.

The natural chaulmoogric (hydnocarpic) acids are characterized by the presence of a cyclopentenyl ring,



and an aliphatic chain varying in length from 1 carbon in the case of aleprolic acid, $\text{C}_5\text{H}_7\text{COOH}$, to 13 in the case of chaulmoogric acid, $\text{C}_5\text{H}_7(\text{CH}_2)_{12}\text{COOH}$.

Recently, several acids having a cyclopropene ring, at or near the center

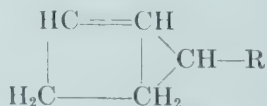


of the hydrocarbon chain have been isolated from natural fats.

Up to the present the aforementioned two homocyclic ring structures are the only ones that have been encountered in fatty acids of natural origin. With the exception of lactobacillic acid they have been found only in the seed fats of plants of tropic and subtropic origin.

(a) Chaulmoogra (Cyclopentenyl) acids

All of the naturally occurring acids of the chaulmoogra group contain from 6 to 18 carbon atoms of which 5 are located in the cyclopentenyl ring. They may be represented by the general structure



in which R is a normal saturated or unsaturated carbon chain containing 1 to 13 carbon atoms. Data for some of the chemical and physical properties of these acids and their ethyl esters are given in Tables 26 and 27.

Chaulmoogra and related oils have been used for centuries in the treatment of human leprosy and other skin disorders. According to statements in the literature the specific action of chaulmoogra oil (*Gynocardia odorata*) was known to the Chinese since ancient times; however, the nature of the fatty acids present in the oil was not understood until the first quarter of the present century. According to Eckey (636) the true

TABLE 26
 Optically Active Acids Found in Chaulmoogra Oils (657)

Acid	Formula	Formula weight	M.p., ° C.	$[\alpha]_D^{25}$, degrees	Iodine value
Chaulmoogric	$C_5H_7(CH_2)_{12}COOH$	280.2	68.5	+60.3	90.5
Hydnocarpic	$C_5H_7(CH_2)_{10}COOH$	252.2	60.5	+69.3	100.7
Alepic	$C_5H_7(CH_2)_8COOH$	224.2	48.0	+77.1	113.4
Aleprylic	$C_5H_7(CH_2)_6COOH$	196.2	32.0	+90.8	129.7
Aleprestic	$C_5H_7(CH_2)_4COOH$	168.1		+100.5 ^a	151.2
Homolog not found	$C_5H_7(CH_2)_2COOH$	140.1 ^a		+110.5 ^a	181.6 ^a
Aleprolic	C_5H_7COOH	112.1		+120.5 ^a	226.7
Gorlic	$C_5H_7(C_{12}H_{22})COOH$	278.2	6.0	+60.7	182.5

^a Calculated.
 TABLE 27
 Ethyl Esters of Optically Active Acids Found in Chaulmoogra Oils (657)

Ethyl ester	Formula weight	B.p., ° C. (10 mm.)	d_{25}^{25}	n_D^{25}	$[\alpha]_D^{25}$, degrees	Iodine value
Chaulmoograte	308.3	222	0.901	1.4592	+55.4	82.5
Hydnocarpate	280.2	200	0.907	1.4578	+61.9	90.5
Aleprate	252.2	174	0.915	1.4562	+66.5	100.7
Aleprylate	224.2	148	0.925	1.4550	+79.1	113.4
Aleprestate	196.2	122 ^a		1.4538 ^a	+86.5 ^a	129.7
Homolog not found	168.1	96 ^a		1.4526 ^a	+94.1 ^a	151.2 ^a
Aleprolate	140.1	70 ^a		1.4514 ^a	+101.8 ^a	181.5
Gorlate	306.3	232	0.912	1.4667	+55.6	167.0

^a Calculated.

chaulmoogra oil comes from the seed of *Hydnocarpus* (*Taraktogenos*) *Kurzii*, a tree which grows in dense forests in Burma and neighboring areas. This oil has been superseded largely by oils from the seeds of *Hydnocarpus Wightiana* from southwestern India and *H. anthelmintica* from Siam, Cambodia, and Cochin China. These oils are also called chaulmoogra oils and sometimes hydnocarpus oils. Similar oils are found in the seeds of other species of the genus *Hydnocarpus* as well as in other genera of the family Flacourtiaceae. Eekey (636, p. 695) lists 17 species belonging to 7 genera which yield seed oils similar to chaulmoogra oil.

All of these oils contain one or more fatty acids having a terminal cyclopentenyl ring, especially chaulmoogric, hydnocarpic, and gorlic acid, which account for 80 to 90% or more of the total fatty acids of these oils.

Other homologs, namely, alepric, aleprylic, aleprestic, and aleprolic acids, were found by Cole and Cardoso (637) to be present in small proportions in some of these oils.

The chaulmoogra acids are optically active owing to the asymmetry of the cyclopentenyl ring. All of the acids exhibit dextrorotation. Reduction of the cyclopentenyl ring destroys the rotation.

Aleprolic Acid, $C_6H_8O_2$. Aleprolic acid, C_5H_7COOH , the lowest homolog of the chaulmoogric acid series, was isolated by Cole and Cardoso (637) from *Hydnocarpus Wightiana* and from *H. anthelmintica*.

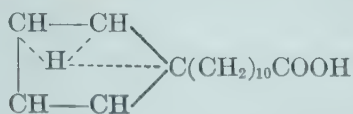
Aleprestic Acid, $C_{10}H_{16}O_2$. Aleprestic acid, $C_5H_7(CH_2)_4COOH$, like aleprolic acid, was isolated in small proportion from the seed oils of *Hydnocarpus Wightiana* and *H. anthelmintica*.

Aleprylic Acid, $C_{12}H_{20}O_2$. Aleprylic acid, $C_5H_7(CH_2)_4COOH$, together with aleprolic and aleprestic acid, was isolated by Cole and Cardoso (637) from the seed oil of *Hydnocarpus Wightiana* and *H. anthelmintica*.

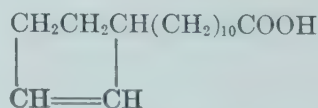
Alepric Acid, $C_{14}H_{24}O_2$. Alepric acid, $C_5H_7(CH_2)_8COOH$, was found as a minor constituent of the seed oils of *Hydnocarpus Wightiana* and *H. anthelmintica*.

Hydnocarpic Acid, $C_{16}H_{28}O_2$. Hydnocarpic acid, $C_5H_7(CH_2)_{10}COOH$, has been reported to constitute 35 to 70% of the total fatty acids of the seed oils of *Hydnocarpus (Taraktogenos) Kurzii* (638), *H. Wightiana* (639), and *H. anthelmintica* (638), and 46% of the fatty acids of the seed oil of sapocainha (*Carpotroche Brasiliensis*) (640).

The acid was first isolated by Power *et al.* (641) in 1904 and between 1904 and 1907 Power and co-workers investigated this acid and the next higher homolog, chaulmoogric. The structure assigned to hydnocarpic acid which involved ring tautomerism was accepted for many years. In 1925, Shriner and Adams (642) reinvestigated the structure of both acids and found that all of their reactions could be accounted for by a single cyclopentenyl ring. They assigned hydnocarpic acid a structure corresponding to 11-(2-cyclopentenyl)-hendecanoic acid which has been accepted ever since. The two structures are illustrated below.



Power and co-workers (641)



Shriner and Adams (642)

On hydrogenation in the presence of platinum, palladium, or platinum-platinum oxide, hydnocarpic acid yields optically inactive dihydrohydnocarpic (11-cyclopentylhendecanoic) acid. The latter acid has been

synthesized by Noller and Adams (643). The dihydro acid melts at 63–63.5° C.

dl-Hydnocarpic acid has been synthesized by Bokil and Nargund (644) by a route involving several changes in a cyclopentane ring. These workers also synthesized several related acids, for example, 3-cyclopentenylpropionic (645). Diaper and Smith (646) synthesized the racemic acid from cyclopent-2-enyl chloride by applying the Robinson–Robinson (647) chain-lengthening method similar to that used by Perkins and Cruz (648) for the synthesis of chaulmoogric acid. Buu-Hoï (649) prepared hydnocarpic acid from chaulmoogric acid by a Barbier-Wieland degradation of ethyl chaulmoograte with magnesium phenyl bromide.

Sacks and Adams (650) prepared homohydnocarpic acid, $C_5H_7(CH_2)_{10}COOH$, by the reduction of ethyl hydnocarpate to the corresponding alcohol, which was converted, via the bromide, to the nitrile. Hydrolysis of the nitrile yielded homohydnocarpic acid containing one more carbon atom than the original acid. The homo acid melts at 56–57° C. and is optically active, $[\alpha]_D + 56.7^\circ$.

Gorlic acid, $C_{18}H_{30}O_2$. Gorlic acid, $C_5H_7(CH_2)_5CH:CH(CH_2)_4COOH$, contains the same number of carbon atoms as chaulmoogric acid but differs from the latter by having an ethylenic linkage between the 6th and 7th carbon atom of the side chain.

The presence in chaulmoogra and similar oils of an acid more unsaturated than chaulmoogric was first suggested by Wrenshall and co-workers (651) in 1924. On hydrogenation of chaulmoogra oil it was found that a dihydrochaulmoogric acid was formed in which the 5-carbon ring was saturated but the side chain contained an ethylenic linkage.

In 1928 André and Jouatte (652) isolated from gorli (*Oncoba echinata*) seed oil an acid, which they named gorlic acid. The same acid was later isolated from gorli seed oil by Cole and Cardoso (653) who established the structure of the aliphatic chain as $-(CH_2)_6CH:CH(CH_2)_4COOH$. These authors investigated the properties of the pure acid and its methyl and ethyl esters. The pure acid is a colorless, practically odorless liquid at ambient temperatures (m.p. 6° C.), with a very marked optical activity, $[\alpha]_D^{25} + 60.7^\circ$.

Cole and Cardoso found gorlic acid to be a constituent of several seed oils of the chaulmoogra group, for example, it was found to comprise 22.8% of the seed oil of *Hydnocarpus (Taraktogenos) Kurzii* (638); 12.3% in *H. Wightiana* (639); 1.4% in *H. anthelmintica* (638); 15.8% in *Carpotroche Brasiliensis* (654); 17.4% in *Calancoba Welwitschii* (655); and 14.8% in *Oncoba echinata* (654).

The presence of gorlic acid in the seed oil of *Carpotroche Brasiliensis* was first reported by Paget (656) who called it dehydrochaulmoogric acid.

Chaulmoogric Acid, $C_{18}H_{32}O_2$. Chaulmoogric acid, $C_5H_7(CH_2)_{12}COOH$, has the greatest molecular weight of the known acids of the chaulmoogra group. It contains 18 carbon atoms of which 13 are in the side chain. Like hydnocarpic acid, chaulmoogric acid was first isolated and studied by Power and co-workers (641) in 1904. These workers assigned to it a tautomeric ring structure similar to that illustrated above for hydnocarpic acid. Shriner and Adams (642) reinvestigated the reactions of chaulmoogric acid and concluded that its structure corresponds to 13-(12-cyclopentenyl)-tridecanoic acid.

Hydrogenation of chaulmoogric acid under the conditions mentioned above for hydnocarpic acid yields optically inactive dihydrochaulmoogric acid (m.p. $70-71^\circ C$). Reduction with zinc and ethanol likewise produces the dihydro acid, but reduction with phosphorus and hydrogen iodide leads to the formation of the hydrocarbon chaulmoogrene, $C_{17}H_{34}$, as a by-product. Reduction with sodium and ethanol yields chaulmoogryl alcohol together with the ester, chaulmoogryl chaulmoograte.

Oxidation of chaulmoogric acid with potassium permanganate yields two dihydroxydihydrochaulmoogric acids melting at 105° and $93^\circ C$. Both acids are optically active, $[\alpha]_D + 11.6^\circ$ and $[\alpha]_D - 14.2^\circ$, respectively.

Chaulmoogric acid adds one mole of bromine to form a dibromide which on debromination yields isochaulmoogric acid. Oxidation of the iso acid with potassium permanganate yields 5-ketooctadecanedioic acid, $HOOC-(CH_2)_3CO(CH_2)_{12}COOH$. When treated with hydrogen bromide in glacial acetic acid, chaulmoogric acid yields bromodihydrochaulmoogric acid (m.p. $36-38^\circ C$). Dehydrobromination yields isochaulmoogric acid.

Chaulmoogric acid has been detected in the seed oil of sapocainha (*Carpotroche Brasiliensis*) of Brazil, in the seed oils of at least seven Asiatic species of *Hydnocarpus*, two species of *Oncoba* of Central Africa, and in the seed oil of *Calancoba Welwitschii* in which it comprises 75% of the total fatty acids.

The separation of chaulmoogric and related acids cannot be accomplished by the usual methods because they appear in both the solid and liquid acid fractions. Because of the anomolous behavior of this group of acids their physical constants were incorrectly reported prior to 1937 when Cole and Cardoso (657) devised new methods of separating and purifying these acids.

dl-Chaulmoogric acid was first synthesized by Perkins and Cruz (658)

in 1927; it was accomplished by condensing the chloride of 11-cyanohen-decanoic acid, $\text{CH}(\text{CH}_2)_{10}\text{COCl}$, with acetoacetic ester, followed by condensation of the reaction product with chlorocyclopent-2-ene. Hydrolysis of the condensation product gave 11-ketochaulmoogric acid, $\text{C}_5\text{H}_7\text{CH}_2\text{CO}(\text{CH}_2)_{10}\text{COOH}$, in 30% yield. Reduction of the keto acid with hydrazine and sodium ethylate under pressure gave *dl*-chaulmoogric acid.

Buu-Hoï and Cagniant (659) prepared the optically inactive dihydro-chaulmoogric (13-cyclopentyl-*n*-tridecanoic) acid by condensing ethyl cyclopentanone-2-carboxylate with ethyl 13-bromo-*n*-tridecanoate which gave 2-ketodihydrochaulmoogric acid. Clemmensen reduction of the keto acid gave dihydrochaulmoogric acid (m.p. 71°C .) identical with the acid obtained by hydrogenation of natural chaulmoogric acid (651).

Stanley and Adams (660) converted hydnocarpic acid to chaulmoogric acid and Hinegardner (661) prepared *dl*-chaulmoogric acid from the natural *d*-isomer, but the *l*-isomer has never been isolated.

Sacks and Adams (650) prepared homochaulmoogric acid by reduction of ethyl chaulmoograte to the corresponding alcohol which was converted, via the bromide, to the nitrile. Hydrolysis of the nitrile gave homochaulmoogric acid, $\text{C}_5\text{H}_7(\text{CH}_2)_{13}\text{COOH}$, containing one more carbon atom than the original acid. The homo acid melted at $66\text{--}67^\circ\text{C}$. and was optically active, $[\alpha]_D + 54^\circ$.

Synthetic Chaulmoogra-like Acids. Because of the belief that the biological activity of the chaulmoogra oils resided in the chaulmoogric-hydnocarpic acids a large number of related compounds were synthesized and their bactericidal activity tested *in vitro* against *Bacillus leprae* and in some cases against *B. tuberculosis* (*Mycobacterium tuberculosis*). The majority of these products were dialkylacetic (α -alkylalkanoic) acids which were prepared by alkylation of diethyl malonate with appropriate halides. A very large number of these and related acids were prepared by Adams and co-workers (662).

A number of these synthetic preparations were equally or more effective than the natural acids when tested *in vitro* against *B. leprae*, but very few of them were tested clinically. One of the latter was ethyl di-*n*-heptyl acetate which was tested on 50 patients. The results indicated that it was not quite as effective as the ethyl esters prepared from the seed oil of *Hydnocarpus Wightiana* (663).

Despite the vast amount of effort which went into the synthesis and testing of these preparations more than a quarter of a century ago, no really effective cure has been found for human leprosy. Recent work has

shown that certain sulfones are equally or possibly more effective than are chaulmoogra preparations prepared from natural oils. Although many claims have been made for the curative value of the chaulmoogra oils, their derivatives, and related synthetics, little unequivocal evidence has been advanced to substantiate them.

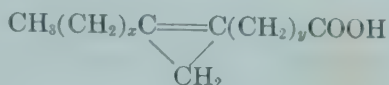
(b) *Sterculic (Cyclopropenyl) Acids*

In recent years several seemingly diverse acids have been isolated from various lipid materials and given names such as malvalic, Halphen, sterculic, and lactobacillic. Investigations into the structures of these acids have revealed the fact that each is characterized by a cyclopropenyl group at or near the center of a long fatty acid chain. Sterculic acid was the first member of this group to have its structure established and since then it has served as a model for comparing and classifying additional related acids. It may, therefore, be used as a class name for those natural acids containing a cyclopropenyl ring in the same manner that chaulmoogra has served for the natural acids containing a cyclopentenyl ring.

Malvalic (Halphen) Acid, $C_{18}H_{32}O_2$. In 1956 Shenstone and Vickery (664) reported the isolation from the lipid fraction of a malvaceous plant, a fatty acid which promoted the development of "pink" whites in the eggs from hens receiving such plants as part of the diet. The unsaturated acid also gave a pronounced Halphen color reaction which is characteristic of cottonseed and kapok oils. The Halphen reaction, which is given by the seed oils of various plants belonging to the Malvaceae, Tiliaceae, and Bombacaceae families, consists in the development of a red color when an oil is heated with carbon disulfide and sulfur in amyl alcohol. In view of the strong Halphen reaction given by the newly isolated acid it was called Halphen acid.

The acid had an iodine value of 110.3, an apparent molecular weight of 283, and its infrared spectra exhibited a prominent band at 1008 cm^{-1} characteristic of a cyclopropene ring. When the acid was fed to laying hens it resulted in pink colorations in 71% of the eggs.

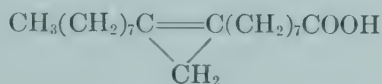
A year later Mcfarlane *et al.* (665) reported a tentative structure for the acid isolated from the seed oils of *Malva verticillata* and *M. parviflora* (666) which they now called malvalic acid. On the basis of the similarity of the infrared spectra of the acid, its methyl ester, and its hydrogenated dihydro derivatives with those for sterculic and lactobacillic acids, they concluded that all three acids contained the same cyclopropene ring and that the structure of malvalic acid corresponded to the formula



where $x + y = 13$.

Dihydrosterculic and dihydromalvalic acids obtained by hydrogenation of sterculic and malvalic acids had no peaks at 1870 cm^{-1} and 1008 cm^{-1} characteristic of the cyclopropene ring. No evidence was found for the presence of an ethylenic bond characteristic of the normal alkenoic acids.

Sterculic Acid, $\text{C}_{19}\text{H}_{34}\text{O}_2$. Sterculic or ω -(2-*n*-octylcycloprop-1-enyl)-octanoic acid comprises more than 70% of the total fatty acids of the seed fat of the Java olive, *Sterculia foetida*, family Sterculiaceae. The acid was isolated in 1941 by Hilditch *et al.* (667) who established its molecular formula as $\text{C}_{19}\text{H}_{34}\text{O}_2$ and proposed for it a structure corresponding to 12-methyl-9,11-octadecadienoic acid, $\text{CH}_3(\text{CH}_2)_5\text{C}(\text{CH}_3):\text{CH}:\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$. Later it was shown by Nunn (668) that sterculic acid contained a cyclopropene ring and that its structure corresponded to the formula



The cyclopropenyl group occupies the 9,10-position instead of a simple ethylenic linkage as in oleic and homologous acids. Mild hydrogenation of sterculic acid yields dihydrosterculic acid identical with lactobacillic acid.

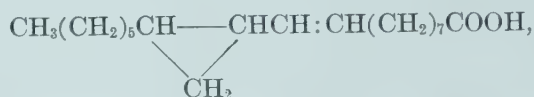
Sterculic acid melts at 18° C . and on reduction with lithium-aluminum hydride in diethyl ether yields sterculyl alcohol melting at 10.6° C . (668).

Sterculic acid and its parent oil (Java olive oil) exhibit a number of unusual properties. For example, both the acid and oil polymerize rapidly even at room temperature, and at 250° C . they polymerize exothermally forming gels (669). The oil and acid give a Halphen test which has been observed with cottonseed, kapok, and baobab oils derived from several species of *Adansonia* found in many parts of Africa. According to Ivanov (670) and Jamieson (671) this reaction is given by the seed oils of many plants belonging to the Malvaceae, Tiliaceae, and Bombacaceae families. This test may be indicative of the presence in these oils of sterculic acid or acids with similar structure.

Oxidation of sterculic acid with permanganate yields hexyl *n*-methyl ketone, heptanoic and azelaic acids (672). Ozonolysis of sterculic acid in cold ethyl acetate followed by hydrogenation the ozonide in the presence

of 30% palladium-charcoal yields 9,11-dioxononadecanoic acid, $\text{CH}_3-(\text{CH}_2)_7\text{COCH}_2\text{CO}(\text{CH}_2)_7\text{COOH}$ (673).

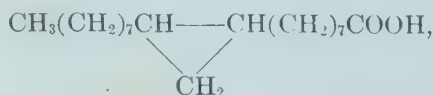
Considerable controversy developed over the structure proposed by Nunn (668) for sterculic acid. This controversy appeared to be revolved by the total synthesis of 9,11-dioxononadecanoic acid by Brooke and Smith (674), Lewis and Raphael (675), and Narayanan and Weedon (676) who found the product was identical with that obtained by Faure and Smith (673) by ozonolysis and hydrogenation of the ozonide of sterculic acid. However, Varma and co-workers (672) continue to maintain the correctness of their originally proposed structure for sterculic acid, namely,



as the only structure which will account for the oxidation products obtained by them and the behavior of the acid toward heat (gelation) and certain olefinic or double bond reagents. Apparently seeds of other members of the Sterculiaceae contain sterculic acid. For example, the seed oil of *Basiloxylon brasiliensis* appears to contain this acid although in somewhat less proportion than *Sterculia foetida* (676a).

Lactobacillic (Dihydrosterculic) Acid, $\text{C}_{19}\text{H}_{36}\text{O}_2$. Lactobacillic or ω -(2-*n*-octylcyclopropyl)-octanoic acid was isolated in 1950 by Hofmann and Lucas (677) from the lipids of *Lactobacillus arabinosus*. They also isolated *cis*-11-octadecenoic (*cis*-vaccenic) acid from the same lipid material. Lactobacillic acid was found to comprise 31% of the total fatty acids of the lipid fraction produced by *L. arabinosus* and 16 to 19% of the total acids from *L. casei*.

The acid melts at 28–29° C., is completely saturated, and contains two less carbon atoms than a normal C_{19} -aliphatic acid. These characteristics suggested that the acid contained cyclopropane ring which appeared to be confirmed on the basis of its infrared absorption spectra. Hofmann and Tausig (678) considered that lactobacillic acid might be identical with phytomonic acid, methyl-*n*-nonadecanoic acid, but other evidence indicates that it is dihydrosterculic acid. The evidence for the latter structure rests on the fact that hydrogenation of sterculic acid converts the cyclopropene ring present in this acid to a cyclopropane ring. The resulting dihydrosterculic acid,



and lactobacillie acid exhibit common properties and hence have been considered to be identical.

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CHAPTER III

ISOMERISM

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Rio de Janeiro, Brazil

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1. Introduction

Many chemical as well as physical properties of the fatty acids depend upon molecular configuration, i.e., upon the mode of arrangement of the component atoms within the molecule. Numerous compounds are known which have the same molecular formulas but exhibit differences in their chemical and physical properties. Such compounds have been found to have different molecular structures or configurations, and are said to be isomeric from the Greek *isos*, equal, and *meros*, part. Isomerism is frequently encountered among the fatty acids and their derivatives (monoesters, glycerides, etc.) and in other lipid materials (alcohols, sterols, ketones, hydrocarbons, phosphatides, etc.) that are found in natural fats and waxes.

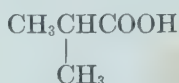
The molecular structure or arrangement of atoms within the molecule may be of several different types, hence correspondingly different forms of isomerism may occur. The principal types of isomerism are the following (1):

(A) Simple structural isomerism

 (a) Nucleus or chain isomerism

- (b) Positional isomerism
- (c) Functional group isomerism
- (B) Stereoisomerism or space isomerism
 - (a) Geometric isomerism
 - (b) Optical isomerism

The differences between isomers included under *structural isomerism* can be adequately expressed by simple structural formulas. For example, *nucleus* or *chain isomerism* results from differences in the arrangement of carbon atoms, as exemplified by butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, and isobutyric acid,

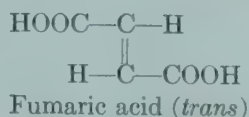
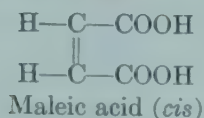


Positional isomerism results from differences in the position occupied by substituent atoms and radicals, or in the position of one or more double or triple bonds in the carbon chain or nucleus. This form of isomerism may be illustrated by three hydroxybutyric acids, namely, 2-hydroxybutanoic, $\text{CH}_3\text{CH}_2\text{CHOHCOOH}$; 3-hydroxybutanoic, $\text{CH}_3\text{CHOHCH}_2\text{COOH}$; and 4-hydroxybutanoic, $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{COOH}$ —or by oleic (9-octadecenoic) acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$; and petroselinic (6-octadecenoic) acid, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$. *Functional group isomerism* is represented by compounds having the same molecular formulas but different functional groups, i.e., they are members of different homologous series. This type of isomerism may be illustrated by methyl-*n*-octyl ketone, $\text{CH}_3\text{CO}(\text{CH}_2)_7\text{CH}_3$, and normal capryl aldehyde, $\text{CH}_3(\text{CH}_2)_8\text{CHO}$. These two compounds have the same molecular formula ($\text{C}_{10}\text{H}_{20}\text{O}$), but different functional groups. This type of isomerism has also been called *metamerism* and the compounds are said to be *metameric*. *Tautomerism* is a special case of functional group isomerism and is best known in the form of *keto-enol isomerism*.

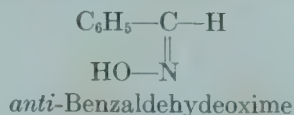
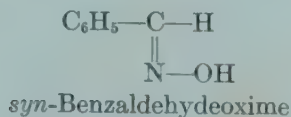
Stereoisomerism or *space isomerism* occurs in compounds having the same molecular formulas and the same functional groups, but which differ in the three-dimensional space arrangement of the carbon atoms within the molecule. One type of stereoisomerism known as *geometric isomerism* arises from the presence within the molecule of a double bond or a ring which prevents free rotation between two unsymmetrically substituted atoms. The double bond coupling may be between similar (carbon-carbon) or dissimilar (carbon-nitrogen) atoms. In the case of carbon-carbon double bonds the pair of geometrically isomeric compounds

are referred to as *cis*- and *trans*-isomers, and in the case of carbon-nitrogen double bonds as *syn*- and *anti*-isomers.

The classical pair of *cis-trans*-isomers is maleic and fumaric acids:



An example of *syn-anti*-isomers is the two benzaldehyde-oximes:



In the normal fatty acids only *cis-trans*-isomerism is encountered but in some derivatives and related compounds, for example, the oximes of the keto acids, *syn-anti*-isomerism can occur.

The phenomenon of *cis-trans*-isomerism was noted as early as 1819 when Poutet (2) converted triolein to trielaidin by treatment of the former with the oxides of nitrogen. The transformation was however, not recognized as one of *cis-trans*-isomerism until many years later.

Geometric isomers always differ in physical properties, in energy content, in stability, and in certain chemical properties. The *cis*-form always has the higher energy content as evidenced by its higher heat of combustion, and hence it is less stable than the *trans*-form. Generally, *cis*- and *trans*-forms and *syn*- and *anti*-forms are relatively easily interconverted although in many cases equilibrium is established between the two forms far short of complete inversion. In the case of oleic (*cis*) and elaidic (*trans*) acids, for example, equilibrium, irrespective of which side it is approached, is established at approximately 66% of elaidic acid.

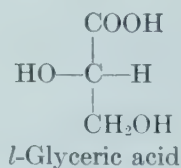
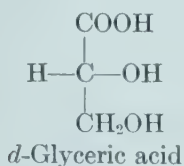
The second type of stereoisomerism, namely, *optical isomerism*, is defined as isomerism in which the isomers differ only in their effect on plane-polarized light, that is, in exhibiting optical activity. Such isomers, irrespective of their physical state (crystalline, solution, pure liquid, or gas) must exhibit optical activity. This activity is observed or measured by passing plane-polarized light through a solution of the compound in a polariscope tube and determining the number of degrees clockwise or counterclockwise the plane of light is turned or rotated. If the rotation is clockwise the compound is said to be dextrorotatory which is indicated by the prefix *dextro* or *d* before the name of the compound. If the rotation is counterclockwise the compound is said to be levorotatory and is indicated by the prefix *levo* or *l* before the name of the compound.

Examination of the nature of these optically active compounds has shown that only those structures possessing mirror images not superimposable upon the original are able to affect plane-polarized light. Such compounds are termed *asymmetric* because their structures are without complete symmetry from the geometric standpoint. Optical activity may arise from *molecular asymmetry* or in the case of some solids from *crystalline asymmetry*.

Crystalline asymmetry has been observed, for example, in quartz and in sodium chlorate. Substances exhibiting crystal asymmetry have a crystal lattice whose mirror image is not identical with the original, hence the *crystal* is asymmetric and rotates plane-polarized light. These substances lose their optical activity when fused or dissolved in a solvent. We are not here concerned with this special form of optical activity, but only that conforming to the definition given above.

Molecular asymmetry and the optical activity resulting therefrom requires that the molecule as a whole be asymmetric or that it contain one or more asymmetric centers. The most common asymmetric center is carbon which is asymmetric when it has four different groups attached to it.

If a molecule is asymmetric, its mirror image will not be identical and the two compounds will constitute a pair of isomers, one dextro and the other levo. Such a pair is termed an *enantiomorphic* pair. An example of such an enantiomorphic pair is the two isomers of glyceric acid which are produced by careful oxidation of glycerol. Glyceric acid contains only one asymmetric carbon center. The structures corresponding to its *d*- and *l*-forms are illustrated below.



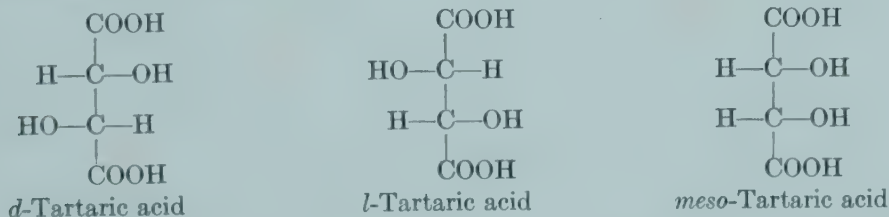
Enantiomorphs differ physically only in their opposite effects on plane-polarized light. The amount of rotation is equal if the concentrations of the two solutions are equal. Generally such enantiomorphs do not differ chemically. An equimolar mixture of two enantiomorphs gives a racemic or *dl*-material which is optically inactive because of external compensation. Both *d*- and *l*-glyceric acid undergo *racemization* with ease either on heating with water alone or in the presence of an organic base such as quinoline, probably via an enol form, to yield a 50:50 or racemic mixture of the *d*- and *l*-forms which is termed *dl*-glyceric acid.

When there are more than two isomers there may be n enantiomorphic pairs: there may be optical isomers which are not mirror images of each other (diastereoisomers); and there may be some isomers which are optically inactive owing to internal compensation (*meso*-compounds).

As an example of the first type there may be cited the 9,10-dihydroxystearic acids produced by the oxidation of oleic and elaidic acids and the 9,10,12,13-tetrahydroxystearic acids produced by the oxidation of linoleic and linoelaidic acids. These hydroxy acids are discussed in detail in Chapter XIII, but it may be stated here that the above-mentioned tetrahydroxy acid contains four different asymmetric carbon atoms and therefore should theoretically have sixteen optical isomers or eight racemic pairs. All eight pairs have been prepared by unequivocal methods and their melting points have been determined.

In the special case of a molecule containing two pairs of similar asymmetric carbon atoms there will be only eight optically active forms existing in four racemic modifications and two additional *meso* forms.

Tartaric acid represents the classical example of optical isomerism with an internally compensated inactive form. The isomeric forms of this acid are illustrated below.



In addition to the *d*-, *l*-, and *meso*-forms of tartaric acid there is a fourth form, namely, the *dl*- or racemic form which arises from an equimolecular mixture of the *d*- and *l*-forms. The racemic form like the *meso*-form is inactive.

2. Structural Isomerism

(a) Nucleus Isomerism

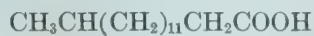
The number of theoretically possible *nucleus* or *structural* isomers of the saturated fatty acids increases with increasing length of the carbon chain, but relatively few such isomers had been detected in natural fats until 1945 when Weitkamp (3) isolated a series of branched-chain acids from wool fat. Since that date increasing numbers of these acids have been isolated from fats, principally of animal origin and generally in

very small proportions. Prior to the work of Weitkamp only isovaleric, tuberculostearic (10-methylstearic), and phytomonic (methylnonadecanoic), and a few incompletely identified acids (phthioic, mycocerotic, etc.) had been isolated from natural lipids. However, a number of branched-chain acids, principally those of low molecular weight, had been synthesized.

Weitkamp's publication was followed by reports by other investigators on the isolation of similar acids from other fats, including butterfat, mutton and ox fats, shark liver oil, the wax glands of the duck and goose, and other lipids. The isolation of these branched-chain acids from natural sources stimulated further work on the synthesis of a large number of similar acids of the saturated (alkanoic) and unsaturated (alkenoic) series. Many of these synthetic acids have been described in the preceding chapter and some of their properties are given in Tables 5 to 8, 20, and 21.

Most of the presently known branched-chain acids from natural sources contain only one branching group, usually methyl, but a few are polyalkyl-branched, and occasionally an acid has been observed with a branching chain other than methyl.

The branched-chain acids isolated by Weitkamp from wool fat comprise two series, one of which is characterized by the presence of a terminal isopropyl residue and has therefore been termed the iso series; the other is characterized by a terminal isobutyl residue and has been termed the anteiso series. In the iso series a branching methyl group is attached at the penultimate position and in the anteiso series at the antepenultimate position, hence the name for the latter series. The two types of structures are represented by the following formulas:



Isohexadecanoic
(isopalmitic)



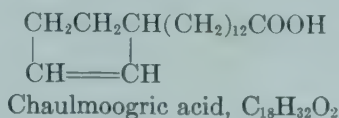
14-Methylhexadecanoic
(anteisopalmitic) acid

The two acids can also be designated as 14-methylpentadecanoic and 14-ethylpentadecanoic, respectively.

Many of the branched-chain acids isolated from natural fats other than wool fat have been found to belong to one or another of these two series. Not all of the acids isolated to date, however, are branched at the penultimate or antepenultimate position. Tuberculostearic acid, for example, is branched at the tenth carbon atom of the chain.

A different type of nucleus isomerism is that observed in the case of

linoleic and chaulmoogric acids, and in linolenic and gorlic acids. As may be seen in the accompanying formulas the first pair of acids have the same empirical formula ($C_{18}H_{32}O_2$), but a different arrangement of carbon atoms and bonds.



Linolenic and gorlic acids are related in the same manner as are linoleic and chaulmoogric acids.

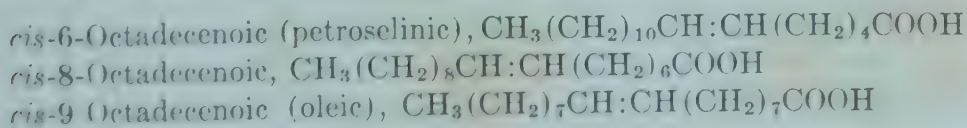
(b) Positional Isomerism

Positional isomerism, resulting from differences in the points of attachment of atoms and radicals, is of rare occurrence in acids derived from natural fats, but is well known in the case of derived and synthetic acids, e.g., in the halogen-substituted, hydroxy, and keto acid series.

Positional isomerism, resulting from differences in the locations of double bonds, is not uncommon among the naturally occurring unsaturated fatty acids and in some instances accounts for marked differences in the properties of a pair of isomers, e.g., between linolenic and eleostearic acids.

Isomeric Alkenoic Acids. Fatty acids containing a single double bond may exhibit two types of isomerism, namely, *positional* and *geometric* isomerism. The first type is represented by variation in the position of the carbon-carbon double bond, and the second by the spatial arrangement of the component parts of the molecule with respect to the double bond.

The number of theoretically possible positional isomers of the normal alkenoic acids increases with the number of carbon atoms in the skeleton. Octadecenoic acid ($C_{18}H_{34}O_2$), for example, can exist in the form of sixteen positional isomers, fifteen of which may exist in two geometric (*cis-trans*) forms. All but a few of the thirty-one of the isomeric octadecenoic acids are known either in the form of natural or synthetic products, or as artifacts produced during hydrogenation of various unsaturated acids. The following isomeric octadecenoic acids have been isolated from natural sources.



trans-10-Octadecenoic, $\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$

cis-11-Octadecenoic, $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$

trans-11-Octadecenoic (vaccenic), $\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$

All of the normal alkenoic acids can exist in similar isomeric forms but, except for the lower members of the series, relatively few are known.

Isomeric Polyenoic Acids. When two double bonds are present in a normal unsaturated acid the total number of isomers, positional and geometric, is greater than when only one double bond is present, but the number of positional isomers is one less than in the alkenoic acids. For example, heptenoic acid ($\text{C}_7\text{H}_{12}\text{O}_2$) can be represented by five positional isomers four of which can exist in two geometric (*cis-trans*) forms or a total of eleven positional and geometric isomers. Heptadienoic acid, containing two double bonds, can exist in four positionally isomeric forms, three of which can exist in four geometrically isomeric forms and one in two geometric forms or a total of fourteen positional and geometric forms.

Despite the greater number of theoretically possible isomers of the dienoic series, fewer isomers, especially of the higher molecular weight acids, are known than in the case of the monoenoic series.

The only octadecadienoic acid that has been isolated from natural fats is linoleic or *cis*-9, *cis*-12-octadecadienoic acid but evidence has been accumulating that other positional and geometric isomers exist in minor proportions in some fats. It has been rather convincingly established that various isomeric octadecadienoic acids are produced by alkali isomerization of natural linoleic acid, by hydrogenation of more highly unsaturated acids, and by dehydration of ricinoleic acid, and other isomers have been prepared synthetically. These products have been discussed in the preceding chapter and will be discussed further under the appropriate reactions by which they are produced.

Positional isomerism has been observed in the trienoic series accompanied and unaccompanied by geometric isomerism. At least four octadecatrichenoic acids have been isolated from natural sources. Two of these acids differ from one another only in the position of the double bonds. The other two differ in the position of the double bonds and also in geometric configuration. Position isomerism in three of these acids may be noted in the following formulas.

6,9,12-Octadecatrichenoic, $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$

Linolenic, $\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$

Eleostearic, $\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_7\text{COOH}$

The fourth isomer, punicic (trichosanic) acid has the same conjugated double bond system as eleostearic acid but a different geometric configuration. Eleostearic acid possesses a structure corresponding to *cis*-9,*trans*-11,*trans*-13-octadecatrienoic, whereas punicic acid corresponds to *cis*-9,*cis*-11,*trans*-13-octadecatrienoic.

Isomeric C₁₆-, C₂₀-, and C₂₂-trienoic acids have also been observed in natural fats. These acids have been described in the preceding chapter.

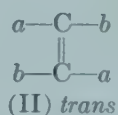
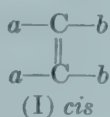
(c) Functional Group Isomerism

Functional group isomerism has not been encountered in naturally occurring fatty acids although acids containing functional groups are known, for example, ricinoleic or 12-hydroxy-9-octadecenoic (C₁₈H₃₄O₂) and licanic or 4-keto-9,11,13-octadecatrienoic (C₁₈H₂₈O₂) acid. These acids are not, however, isomeric because they do not have the same empirical formulas.

3. Stereoisomerism

(a) Geometric Isomerism

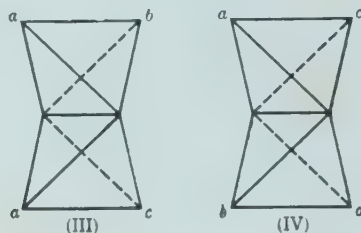
Geometric or *cis-trans*-isomerism, one of the two forms of stereoisomerism, is a characteristic property of the unsaturated fatty acids. The structural relationships of this type of isomerism when of the simplest form, i.e., involving only a single carbon-carbon double bond, may be illustrated as follows:



In the hypothetical compounds illustrated above, the one with two similar groups on the same side of the double bond is referred to as the *cis*-isomer (I) and the other as the *trans*-isomer (II).

The spatial arrangements of the two isomers become more evident when they are considered from the geometric point of view. If the carbon atom is presumed to have a tetrahedral structure, two carbons can be joined by a single bond situated at the common apex of a pair of tetrahedrons about which free rotation can occur. If, on the other hand, a double bond is shared by two carbon atoms it can be represented as occurring at a common edge of two tetrahedrons and free rotation would be prohibited or restricted by the rigidity of the structure.

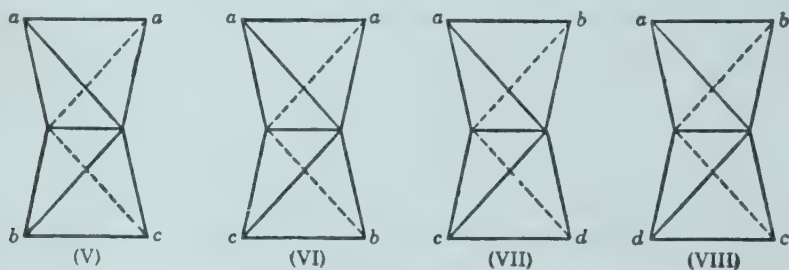
In one of these structures it is evident that the two *a* groups are closer together (III) than they are in the other (IV). If a plane is passed



Carbon-carbon double bonds.

through that edge of the tetrahedrons which is shared between them and continued in each direction so as to bisect the lines joining the *a* and the *b* or *c* group, the similar groups are either on the same side of the plane, i.e., in the *cis*-position (III), or they fall on opposite sides of this plane and are in the *trans*-positions (IV). The four groups (*abcd*) fall in one plane, hence the mirror image of each form is identical with the object, and no optical isomers can exist in this series.

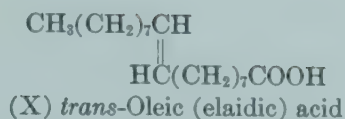
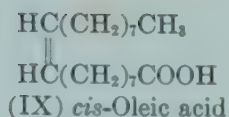
It can also be seen that each of the atoms joined by the double bond must be unsymmetrically substituted. When one of the atoms carries two *a* groups, and is thus symmetrical (V and IV), the two molecules are superimposable, and hence do not represent isomers. Even though all



Carbon-carbon double bonds (1).

four attached groups are different (VII and VIII), only one pair of isomers is possible.

Instead of using tetrahedrons, it is more convenient to represent the structural relationships of the *cis-trans*-isomers by the condensed formulas illustrated in (I) and (II). The two forms of 9-octadecenoic can be represented by these condensed formulas as shown in (IX) and (X).



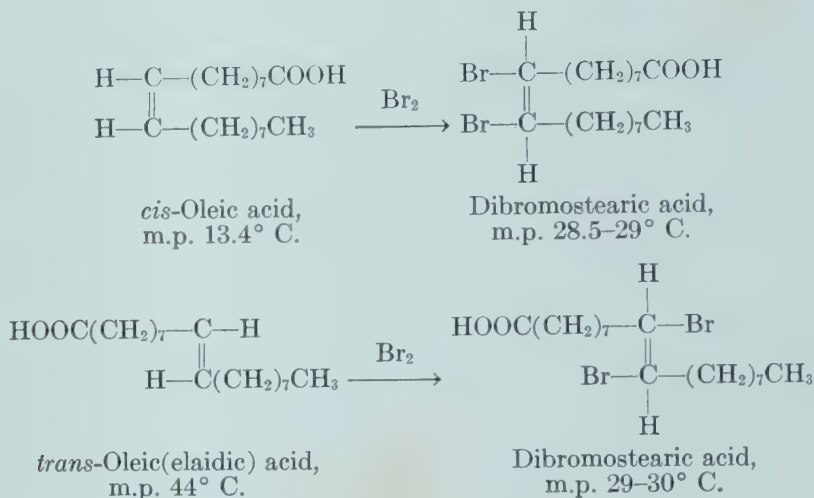
It has been observed from a study of various *cis-trans*-isomers whose configurations have been established that there is a surprising regularity in the difference in physical properties between the *cis*- and *trans*-forms. The *cis*-form usually has the lower melting point, the greater solubility in inert solvents, the higher heat of combustion, and in the case of acids, the higher ionization constant. The unsymmetrical *cis*-form exhibits a considerably higher dipole moment than the more symmetrical *trans*-form. The x-ray spacing of the *cis*-form is shorter than that of the *trans*-form. The *cis*-form is generally, although not always, found in nature, and the *trans*-form is generally produced by treatment of the *cis*-form by chemical and physical agents. In most cases the *cis*-form is labile and the *trans*-form stable, but if the two forms are of the same approximate stability, equilibrium inversion will occur by proper treatment of either form.

Alkenoic Acids. All of the normal alkenoic acids except those having a double-bonded terminal carbon atom can exist in the two geometric forms illustrated by oleic and elaidic acid. In general, only the *cis*-form is encountered in natural fats, but in few cases, for example, *trans*-11-octadecenoic acid, both forms have been observed.

The natural *cis*-acids can be converted to the corresponding *trans*-acids by treatment of the former with appropriate reagents such as oxides of nitrogen (mercury and nitric acid), sulfur, selenium, etc. Griffiths and Hilditch (4) established the fact that the *cis-trans*-transformation (oleic-elaidic) is an equilibrium reaction which is completely reversible so that equilibrium mixture is attained regardless of the nature of the isomer used. For the oleic-elaidic transformation, equilibrium is attained at 66% of elaidic acid.

When the double bonds of *cis*-oleic acid and *trans*-elaidic acid are saturated with hydrogen, the same stearic acid is obtained, whereas the addition of halogens results in the formation of different dihalogenated stearic acids. Treatment of oleic and elaidic acids with bromine produces two isomeric dibromostearic acids melting at 28.5–29° C. and 29–30° C., respectively. On debromination with zinc and alcoholic hydrogen chloride each dibromo compound reverts exclusively to the acid from which it was prepared. It is, therefore, evident that the bromine has entered the molecules of oleic and elaidic acids at the same position on the carbon tetrahedrons which were previously united in a double bond.

and so-called *cis*-addition has occurred. These stereochemical relationships may be represented as follows:



It has long been recognized that oxidation of maleic acid with alkaline potassium permanganate leads to the formation of mesotartaric acid, while similar treatment of fumaric acid produces *dl*-tartaric acid. The hydroxyl group enters the molecule at the same positions on the carbon tetrahedrons that were previously united in a double bond and *cis*-addition occurs in a manner analogous to the bromine addition to oleic and elaidic acids.

When the dibromostearic acids produced by the addition of bromine to oleic and elaidic acids are treated with aqueous or alcoholic potash, two isomeric dihydroxystearic acids are formed which melt at 95° and 132° C. , respectively. The structures of the hydroxy acids correspond to those of the original *cis*- and *trans*-oleic acids. Oxidation of oleic and elaidic acids with peracetic or other per acids results in the formation of the same two dihydroxy stearic acids melting at 95° and 132° C. , respectively. All of these reactions represent *cis*-additions, but *cis*-addition does not always occur, especially under certain conditions of oxidation. For example, when oleic and elaidic acids are oxidized in alkaline media, especially with ice-cold aqueous alkaline potassium permanganate, the products of oxidation are exactly the reverse of those produced by peracid oxidation, oleic acid yields dihydroxystearic acid melting at 132° C. and elaidic acid yields a dihydroxystearic acid melting at 95° C. (5). Alkaline permanganate oxidation of oleic and elaidic acids, therefore, represents *trans*-addition. The reaction mechanisms by which the various

isomeric hydroxy acids are produced under different conditions of oxidation are discussed in Chapter XIII.

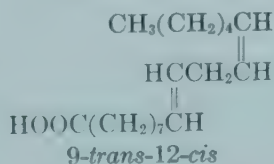
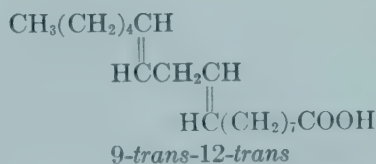
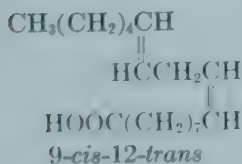
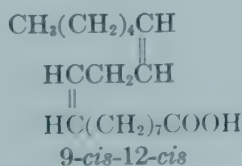
Geometric isomers of the alkenoic acids are also produced during hydrogenation of polyunsaturated acids and their monoesters and glycerides. The iso acids produced under different conditions of catalytic hydrogenation are mixtures of positional and geometric isomers resulting from saturation of specific double bonds, the shift of bonds along the carbon chain, and inversion at a double bond as a result of hydrogenation-dehydrogenation reactions.

Alkadienoic Acids. When more than one unsymmetrically substituted double bond is present in a molecule, the number of geometric or *cis-trans*-isomers can be determined by writing out the possible structures. If the groups attached to the double-bonded carbon atoms are such that all of the ethylenic units are *dissimilar*, the number of possible isomers is 2^n , where n is the number of ethylenic linkages. Thus, the compound $ab-C=CR-CR=C-cd$ can exist in four *cis-trans*-forms.

Only a very few diethenoic acids have been isolated from natural fats; one of these, namely, 2,4-decadienoic acid, contains a conjugated system of double bonds, the others contain only isolated double bonds and all of them possess *cis*-configurations.

The most important and best-known diethenoic acid is linoleic or 9,12-octadecadienoic acid. Considerable evidence is extant to indicate that other octadecadienoic acids are present in some natural fats but whether these are positional or geometric isomers is not certain.

If the rule mentioned above is applied to linoleic acid it is evident that the theoretically possible number of geometric isomers is 2^2 or 4. The configurations of the four possible geometric isomers may be represented as follows:



The fact that four 9,12-octadecadienoic (linoleic) acids are possible of existence and that each of these four isomers can give rise to four opti-

cally active tetrabromo- and tetrahydroxystearic acids resulted for many years in confusion concerning the identity of the known linoleic acids. In 1939, Riemenschneider *et al.* (6) on the basis of theoretical considerations concluded that the number of tetrabromo- or tetrahydroxystearic acids that would be obtained by bromination or oxidation of a given geometric isomer would be two instead of four. The basis for this conclusion is illustrated in the formulas XI to XVI.

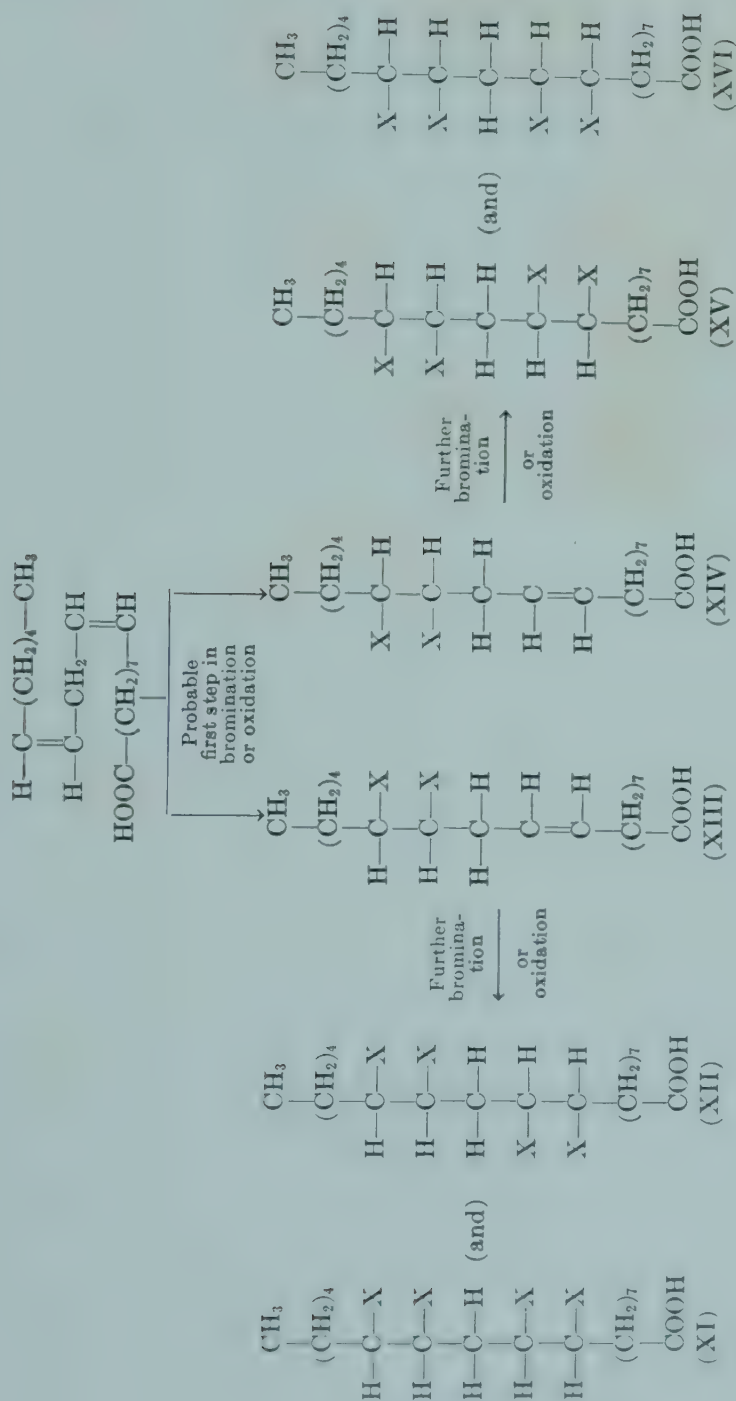
The addition of bromine to *cis*-9,*cis*-12-octadecadienoic (α -linoleic) acid is assumed to occur in two steps with formation of two intermediate bromination products (XIII) and (XIV) which undergo further bromination to give products (XI), (XII), (XV), and (XVI). Since products (XI) and (XVI) and products (XII) and (XV) represent optical isomers, each pair of isomers would produce one racemic acid and, therefore, only two tetrabromo- and two tetrahydroxystearic acids should result from bromination or oxidation of the original α -linoleic acid.

If the same reasoning is applied to *trans*-9,*trans*-12-octadecadienoic (linolelaidic) acid, there would likewise result but two ultimate products of bromination or oxidation. In this case they would represent the racemates of the optically isomeric pairs of acids represented by formulas (XI) and (XII), and (XV), and (XVI), respectively.

Each of the four geometric isomers of linoleic acid should similarly yield two racemic tetrabromo- and tetrahydroxystearic acids or a total of eight racemic pairs corresponding to the sixteen optical isomers derivable from the four geometric isomers.

The same conclusions concerning the identity of these isomers were arrived at independently by McCutcheon and co-workers (7), and in the case of the tetrahydroxystearic acids they were subsequently verified experimentally by McKay and Bader (8) who prepared all eight racemic pairs.

Naturally occurring α -linoleic (*cis*-9,*cis*-12-octadecadienoic) (m.p. -5° to -5.27° C.) is characterized by the fact that on bromination it yields a solid tetrabromostearic acid melting at 115.5° C. and a liquid tetrabromostearic acid in an approximate ratio of 1:1. On oxidation with alkaline potassium permanganate it forms two tetrahydroxystearic acids which have been designated α -sativic (m.p. 164° C.) and β -sativic (m.p. 174° C.), respectively. According to Riemenschneider *et al.* (6) the tetrahydroxystearic acid melting at 157 – 159° C., which has frequently been reported to be present among the oxidation products of α -linoleic acid, is a eutectic mixture of the above-mentioned two sativic acids. On the basis of the analogy with the oxidation products of oleic acid, the



aforementioned sativic acids represent *trans*-addition products. Oxidation of α -linoleic acid in an acid medium, e.g., peracetic or other peracids, produces two additional tetrahydroxystearic acids which have been designated γ -sativic (m.p. 126° C.) and δ -sativic (m.p. 148° C.), respectively. In this case, also in analogy with oleic acid, the formation of the latter sativic acids from α -linoleic acid represents *cis*-addition.

When α -linoleic acid is isomerized (elaidinized) with oxides of nitrogen or selenium it is transformed in part to linolelaidic or *trans*-9,*trans*-12-octadecadienoic acid (m.p. 28 – 29° C.). Kass and Burr (9) found that the elaidinization reaction produced only 16% linolelaidic acid. On bromination linolelaidic acid gave a crystalline tetrabromostearic acid melting at 78° C. and a second liquid tetrabromostearic acid. On oxidation of linolelaidic acid there were obtained two tetrahydroxystearic acids melting at 122° and 146° C., respectively. These two products obviously corresponded to γ -sativic (m.p. 126° C.) and δ -sativic (m.p. 148° C.) acids which are obtained from α -linoleic acid on peracetic oxidation.

These authors also isolated from the products of the elaidinization reaction a liquid fraction which on bromination gave no solid tetrabromide, but which on oxidation with alkaline permanganate gave two tetrahydroxystearic acids melting at 126 – 127° and 156 – 158° C. They concluded that the liquid portion of the elaidinization products comprised a partially isomerized linoleic acid which was either *cis*-9,*trans*-12- or *trans*-9,*cis*-12-octadecadienoic acid or a mixture of the two. In the light of the work of McKay and Bader (8) they may have corresponded to ϵ -sativic (m.p. 126°) and ζ -sativic (m.p. 164° C.) acids.

In addition to the widely occurring α -linoleic acid, considerable evidence, for the most part indirect, has been accumulating which seems to point to the presence of other isomeric linoleic acids in some fats. The existence of these acids is usually predicated on the fact that they do not yield the bromination and oxidation products which are characteristic of α -linoleic and linolelaidic acids. On the other hand, they yield, at least in some cases, caproic and azelaic acids on disruptive oxidation which would seem to rule out the possibility that they are positional isomers of 9,12-octadecadienoic acid.

For example, Suzuki and Inoue (10) isolated a linoleic acid from the fat of silkworm pupae which did not yield an insoluble tetrabromide and was, therefore, designated isolinoleic acid. When reduced with one mole of hydrogen it apparently yielded normal *cis*-oleic acid, since the latter acid on oxidation gave dihydroxystearic acids identical with those obtained from oleic acid under the same conditions of oxidation. The oleic

acid produced by partial hydrogenation of the isolinoleic acid gave elaidic acid on isomerization. When normal α -linoleic and the isolinoleic acids were hydrogenated in two stages the absorption of hydrogen occurred more rapidly with the normal than with the iso acid in both stages.

Smith and Chibnall (11) isolated from cocksfoot and perennial ryegrass a linoleic acid which gave a liquid but no crystalline tetrabromide. The oily bromination product contained 52.6% of bromine compared to 53.3% required by theory for $C_{18}H_{32}O_2Br_4$. Only a very small amount of sativic acid was obtained on oxidation. The authors concluded that the linoleic acid isolated from the two grasses comprised a mixture of isomeric linoleic acids together with a small proportion of α -linoleic acid.

As mentioned in the preceding chapter isomeric octadecadienoic acids have been reported to be present in small amounts in codliver and whale oils, butterfats, milk fat, and in the liver and depot fats of beef cattle and sheep. Whether or not these products are positional or geometric isomers of α -linoleic acid is not known.

Kass *et al.* (12) examined corn, cottonseed, peanut, poppyseed, sunflowerseed, coconut, olive, and almond oils, and cocoa butter with respect to their content of linoleic acid and concluded that only one octadecadienoic acid was present in these oils, although the yield of tetrabromostearic acid varied from 27 to 51% of the amount calculated to be present on the basis of the iodine-thiocyanogen determination. These authors concluded that the variation in the recovery of tetrabromostearic acid was due to the unreliability of the "insoluble bromide" method rather than to the presence of isomeric linoleic acids which failed to give insoluble derivatives on bromination. It is generally agreed that the insoluble bromide method is limited in its applicability, especially from the quantitative point of view, but other evidence exists which seems to indicate that some oils do contain isomeric octadecadienoic acids.

Frankel *et al.* (13) prepared linoleic acid from corn, sesame, cottonseed, grapeseed, and poppyseed oils by low-temperature crystallization and concluded that in each case the acid was identical with α -linoleic acid prepared by debromination of α -tetrabromostearic acid. When the crystallization procedure was applied to olive oil, the linoleic isolated gave abnormally low yields of the high melting of α -tetrabromostearic acid, and the acid itself had an appreciably lower melting point than the corresponding acid isolated from other vegetable oils. They, therefore, concluded that olive oil contains a mixture of isomeric linoleic acids in which α -linoleic acid predominates.

Some of the confusion surrounding the existence of isomeric octadeca-

dienoic acids has undoubtedly resulted from the limitations of the older methods used in isolating and purifying the components of mixtures of unsaturated fatty acids having the same or nearly the same molecular weight and very closely related physical properties.

It is also significant that the linoleic acids, isolated from natural sources, which fail to respond to the tetrabromide test are almost always present as minor components and oftentimes represent an insignificant portion of the total mixed fatty acids or of the total unsaturated fatty acid fraction.

It is now realized that at every step in the isolation and purification of polyethenoid acids from natural sources alteration of their structure can occur unless meticulous care is observed to avoid such changes. These alterations include oxidative changes, shifting of the double bond, especially to form conjugated systems, polymerization, cyclization, etc. It is also recognized that the yield of insoluble tetrabromostearic acid, which is obtained on bromination of the mixed unsaturated fatty acids, may be markedly affected by the nature and amount of other acids and bromo derivatives that are present in the mixture. It is possible, therefore, that some of the anomalous behavior, which has been recorded with respect to certain naturally occurring linoleic acids, may be explained by past limitations of the preparative and analytical methods rather than on the basis of the existence of isomeric, and especially geometrically isomeric, linoleic acids.

Furthermore the older methods were not sufficiently specific to permit the separation of closely related isomers, especially when present in very small proportions. Application of more recently developed techniques (urea complex formation, chromatography, extended distillation, etc.) of separation and purification coupled with more sensitive methods of analysis (spectrophotometry, etc.) will probably reveal the existence of suspected isomers in some of these fats and perhaps in other fats in which they were heretofore unsuspected.

Alkatrienoic Acids. Since the number of geometric isomers of the polyethenoid acids which are possible of existence increases exponentially with the number of double bonds, each positional isomer of the triethenoid series can exist in 2^3 or 8 different forms. Two of these forms would be represented by *cis-cis-cis*- and *trans-trans-trans*-configurations and the other six forms by various *cis-trans*-configurations.

Of the eight possible geometric forms of linolenic acid, $\text{CH}_3\text{CH}_2\text{CH:CHCH}_2\text{CH:CHCH}_2\text{CH:CH}(\text{CH}_2)_7\text{COOH}$, only the natural acid and the corresponding completely elaidinized isomer are known with certainty.

The natural form of the acid has been shown by infrared spectrophotometry to be *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid (14,15) and the completely elaidinized acid produced by treating the former with oxides of nitrogen has been shown by the same method to be *trans*-9,*trans*-12,*trans*-15-octadecatrienoic acid (15).

The chemical methods that were originally used to establish the geometric structures of α -linolenic and elaidolinolenic acids paralleled those applied to linoleic acid, and the results were more difficult to interpret. Not only was it difficult to prepare the natural acid in highly pure form, but it was not realized that since the hexabromo and hexahydroxy derivatives of linolenic acid possess 6 asymmetric carbon atoms they can be represented by 64 optical isomers and 32 racemic pairs. Failure to recognize the multiplicity of theoretically possible isomeric bromo and hydroxy derivatives, coupled with the inability to prepare linolenic acid in highly pure form, resulted in controversy and conflicting interpretation of experimental results.

The naturally occurring linolenic acid produces, on bromination, a solid, or α -hexabromostearic acid, melting at 185° C. (16) and a liquid, or β -hexabromostearic acid. On oxidation with alkaline potassium permanganate, α -linolenic acid produces two hexahydroxystearic acids which are designated as linusic (m.p. 203° C.) and isolinusic acid (m.p. 173–175° C.). Erdmann and Bedford (17) obtained a 25% yield of the solid, or α -hexabromostearic acid, and 75% of the liquid, or β -hexabromostearic acid, when they brominated linolenic acid, originally obtained by debrominating the solid hexabromide. They therefore considered the original debrominated acid to be a 1:3 mixture of α - and β -linolenic acids. Rollet (18) disputed this view and assumed that the linolenic acid obtained by debromination of the solid hexabromide was a homogeneous substance identical with the naturally occurring acid, and that on rebromination four pairs of racemic hexabromostearic acids were produced, only one of which was an ether-insoluble crystalline product. Rollet, and also McCutcheon (19), claimed that both the solid, α -, and the liquid, β -hexabromostearic acids produced the same linolenic acid on debromination, and that the regenerated acid formed the same hexabromo- and hexahydroxystearic (linusic) acids as did the natural acid.

Shinowara and Brown (20) prepared linolenic acid from linseed and perilla oils which, on the basis of analytical data, represented a maximum purity of 88% on the assumption that the impurity was linoleic acid. This acid yielded 30 to 36% of hexabromostearic acid, rather than 25% claimed by most workers.

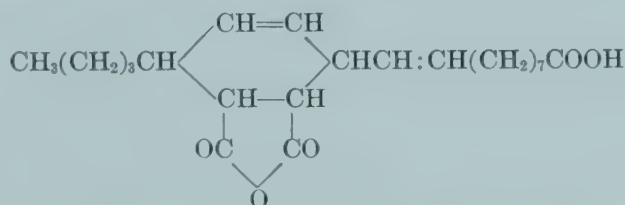
These workers, as well as Matthews, Brode, and Brown (21), concluded from a comparative investigation of the properties of the natural acid prepared by low-temperature crystallization, and the acid recovered by debrominating α -hexabromostearic acid, that the two were not identical, and that the debrominated acid consists of a mixture of isomeric linolenic acids. They further concluded that the linolenic acid produced by debrominating α -hexabromostearic acid contains 12 to 15% of a *cis-trans*-isomer which yields no petroleum ether-insoluble or diethyl ether-insoluble hexabromide. Furthermore, Matthews *et al.* found that while the properties (melting point, refractive index, hexabromide value, etc.) of various specimens of linolenic acid obtained by debromination of the solid hexabromide were similar, those of the acids produced from linseed oil and perilla oil by low-temperature crystallization varied, and depended on the oil from which the acid was derived. For these reasons, they concluded that the linolenic acids from these two oils were not identical and represented mixtures of isomeric acids and in both cases differed from the linolenic acid produced by debromination of α -hexabromostearic acid.

In contrast to the attention given linolenic acid, little work has been done on the solid geometric isomer, elaidolinolenic acid. This isomer has been prepared by Kass, Nichols, and Burr (22) by heating the ethyl ester of the naturally occurring acid with selenium for 17 hours at 205–215° C. The regenerated and purified elaidolinolenic acid melted at 29–30° C. and gave a hexabromostearic acid melting at 169–170° C. The ethyl ester of the hexabromide melted at 114–115° C. On the basis of a 31% yield of solid hexabromostearic acid (m.p. 169–170° C.) from elaidolinolenic acid and similar yields of hexabromostearic acid (m.p. 181.0–181.5° C.) from natural linolenic acid, Kass and co-workers concluded that bromination of linolenic acid resulted in the formation of three pairs of racemic hexabromostearic acids instead of four, as was postulated by Rollet (18). Formation of the fourth pair was assumed to be impossible owing to stearic hindrance. They further concluded, from the nature of liquid bromides in the bromination products of their elaidolinolenic acid, that there remained no demonstrable proof for the existence of β -linolenic or isolinolenic acids in drying oils. For a discussion of the hexahydroxy-derivatives of linolenic acid the reader should consult Chapter XIII.

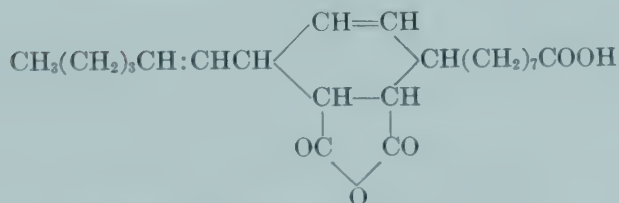
Conjugated Trienoic Acids. Several conjugated trienoic acids have been observed in natural fats. The first and best known of these acids is eleostearic or 9,11,13-octadecatrienoic acid. It is a position isomer of linolenic acid but differs from the latter in many of its chemical and physical properties. It contains three double bonds, hence it can exist in

eight *cis-trans*-, or geometrically isomeric, forms. Natural α -eleostearic acid (m.p. 48–49° C.), on exposure to light, especially in the presence of a trace of iodine or other isomerizing catalyst, passes to a higher melting β -form (m.p. 71° C.). A third isomer (m.p. 44° C.), known as puniic (trichosanin) acid, has also been found as a constituent of several plant fats. This acid, like α -eleostearic acid, is converted under the influence of light and isomerizing catalysts to β -eleostearic acid. Each of these acids has been shown to be a 9,11,13-octadecatrienoic acid; and hence they must differ from one another only in their geometric configurations.

Conversion of these acids to their bromo and hydroxy derivatives does not yield useful information concerning their geometric configurations. Morrell and co-workers (23) found that the α - and β -forms of eleostearic acid react with maleic anhydride to produce two different diene addition products, melting at 62.5° and 77° C., respectively. According to these workers, the maleic anhydride condensation products of the α - and β -acids have the following structures:



α -Eleostearic diene product, m.p. 62.5° C.



β -Eleostearic diene product, m.p. 77° C.

Extensive investigation of the oxidation products of the diene adducts of these acids by Morrell *et al.* and other workers did not lead to the assignment of the correct structures to these acids. The problem was finally resolved by the application of infrared spectrophotometry to the diene adducts and the free acids, the results of which indicated that α -eleostearic acid is *cis*-9,*trans*-11,*trans*-13- and β -eleostearic acid is *trans*-9,*trans*-11,*trans*-13-octadecatrienoic acid (24).

Isomerization of the natural acid to the β -form consists, therefore, in an inversion at the double bond attached to the 9th carbon atom to form the all *trans*-product. Although the earlier workers established the fact that

diene addition occurred at the 11th and 14th carbon atoms in the natural acid and at the 9th and 12th carbon atoms in the isomerized acid, they failed to recognize that such addition occurred only at the *trans*-portion of the molecule.

Punicic acid, the third isomer of 9,11,13-octadecatrienoic acid, does not react with maleic anhydride to form a diene adduct (25); therefore it cannot contain two adjacent transethenoid groups. Ahlers *et al.* (26) concluded from infrared spectrophotometric analysis that punicic acid possesses a *cis,cis,trans*-configuration and probably is *cis-9,cis-11-trans-13*-octadecatrienoic acid and that trichosanic acid has the same configuration (27). Isomerization of punicic (trichosanic) acid to β -eleostearic acid therefore involves inversion at the two *cis*-ethenoid groups.

Licanic or 4-keto-9,11,13-octadecatrienoic acid is, like all the related triethenoic fatty acids, capable of existing in eight geometrically isomeric forms. Two such forms are known, namely, α -licanic acid (m.p. 74–75° C.) and β -licanic acid (m.p. 99.5° C.). The α -form, which occurs in oiticica, po-yoak, and other oils, passes to the β -form on exposure to light in the presence of traces of iodine or sulfur. The two forms of licanic acid are also distinguished by differences in their derivatives. α -Licanic acid yields a semicarbazone, melting at 110–111° C., and a maleic anhydride addition product, melting at 79° C., whereas β -licanic acid gives a semicarbazone, melting at 138° C., and a maleic anhydride adduct, melting at 97° C. (28). Analysis of the infrared spectra of α - and β -licanic acids indicates that their geometric configurations correspond to those of α - and β -eleostearic acids, namely, *cis-9,trans-11,trans-13*- and *trans-9,trans-11,trans-13*-. The licanic acids, therefore differ from the eleostearic acids only in having a ketonic oxygen attached at the 4th carbon atom.

Parinaric acid or 9,11,13,15-octadecatetraenoic acid contains four double bonds and hence is capable of existing in 2⁴ or 16 geometrically isomeric forms. Actually only two forms are known, namely, α -parinaric acid (m.p. 85–86° C.), which occurs naturally in the seed fat of *Parinarium laurinum*, and β -parinaric acid (m.p. 95–96° C.), which is produced by the action of light on the α -form in the presence of a trace of iodine. Examination of the infrared spectra of α - and β -parinaric acids led Ahlers *et al.* (15) to conclude that the β -form of the acid possesses an all *trans*-configuration, and that the α -form contains either two *cis*- and two *trans*-, or one *cis*- and three *trans*-ethylenic groups.

(b) Optical Isomerism

Optical isomerism, which is detected by measuring the degree to which a given substance is capable of rotating a plane of polarized light, occurs

in compounds having no complete symmetry from a geometric standpoint. The structural configurations of *asymmetric* molecules are such that one molecule is not identical with its mirror image. Such molecules and their mirror images are identical in all respects in their chemical and physical properties except in their ability to rotate a plane of polarized light. Optical activity occurs in: (a) compounds containing one or more asymmetric atoms, and (b) compounds which contain no individual asymmetric atoms but in which asymmetry is due to the absence of any of the necessary elements of symmetry that permit the mirror image of the molecule to be superimposable.

The isomer that rotates a plane of polarized light to the right is designated as *dextrorotatory* and the one that rotates it to the left is designated as *levorotatory*. The optical activity of both isomers is the same in degree but opposite in sign. The two forms are often referred to as *enantiomorphs*. When equal amounts of the *dextro*- and *levo*-isomers are mixed, the resulting product will show no activity because the optical effect of one form is neutralized by that of the other. Such a product is known as a *racemic* modification and is designated as *dl*-form. Most synthetic preparations are *dl*-modifications, since the reactions by which they are formed result in the production of equal amounts of each isomer. Generally, *racemates* differ in many respects from their optically active isomers and in many cases they can be resolved into their component *d*- and *l*-forms.

A compound which would otherwise exhibit optical activity may be optically inactive owing to internal compensation. If the compound contains two asymmetric carbon atoms, one of which is dextrorotatory and the other levorotatory by exactly the same amount, the net rotation will be zero and the compound is inactive. Such compounds are designated as *meso*-forms. The *meso*-form of a compound differs from its *dl*-form in physical properties, and both the *meso*- and the *dl*-forms differ from the individual *d*- and *l*-forms.

If a compound contains several asymmetric carbon atoms the optical rotation of the compound as a whole will be the algebraic sum of the individual rotations. The resultant sum of these rotations, which individually may be relatively large, may be an immeasurably small value. Unfortunately, there is no known method whereby the absolute rotation of a single asymmetric carbon atom can be determined in a compound containing two or more asymmetric carbon atoms.

The optical activity of a compound may be expressed as specific rotation, $[\alpha]$, or molecular rotation, $[M]$. The specific rotation of an opti-

cally active liquid was originally defined as the rotation produced by a layer of active substance one decimeter in length, or if a solution, of one gram of active substance in a volume of one cubic centimeter. However, the density of the liquid must be taken into account, therefore, the specific rotation, $[\alpha]$, at a temperature, t , and definite wavelength of light is expressed as

$$[\alpha]_{\lambda}^t = r/l_d,$$

where r equals the observed polarimetric rotation in degrees, l , the length of the column, and d , the density; or in the case of a solution,

$$[\alpha] = rv/lp,$$

where v equals the volume in cubic centimeters and p the grams of substance contained in v volume of the solution.

In order to intercompare the optical rotations of various substances, it is necessary to convert specific rotations to molecular rotations. The molecular rotation calculated on the basis of gram-molecular weights may be a very large value, and for convenience this value divided by 100 is used in expressing the molecular rotation $[M]$. The molecular rotation is, therefore, expressed as

$$[M]_{\lambda}^t = m/(100 \cdot rv)/lp,$$

where m is the molecular weight of the substance and the other symbols have the same significance as in the case of specific rotation.

All of the known optically active natural or synthetic fatty acids are branched-chain or substituted acids. The natural acids are generally, although not always, dextrorotatory, whereas both levo- and dextrorotatory acids have been prepared synthetically. Substituted acids, such as bromo and hydroxy, produced by bromination or oxidation of natural unsaturated acids, are racemic mixtures and, therefore, inactive.

Prior to 1929 only a few optically active acids had been isolated from natural fats. Most of these were mono- and dihydroxy acids. Exceptions to this statement are the cyclopentenyl-substituted chaulmoogric and hydnocarpic acids isolated as early as 1904.

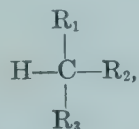
The isolation of tuberculostearic (10-methylstearic) acid by Anderson and Chargoff (30) in 1929 was soon followed by reports of the isolation of other optically active branched-chain acids, e.g., phthioic (31) in 1936, mycocerosic (mycoceranic) (32) and phytomonic (33) in 1944. The physiologically important hydroxy acid, cerebronic (34) had been isolated in 1901 and hydroxynervonic acid (35) in 1926, both from brain

lipids. These were followed by the isolation of mycolic acid (36) from human tubercle bacilli in 1938. The isolation of these optically active and physiologically important hydroxy and branched-chain acids stimulated an interest in the synthesis and study of related synthetic acids.

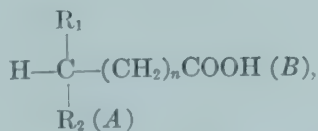
Synthetic Acids. Prior to 1929 various optically active derivatives of the higher molecular weight normal fatty acids had been prepared in which the activity is derived from the introduced radical. Optically active amyl, bornyl, and methyl esters and the brucine and cinchonine salts of the normal aliphatic acids had been prepared and their molecular rotations determined (37). Derivatives of this type are, however, unrelated to the optically active acids isolated from natural lipids.

One of the earliest and most active group of investigators who were to contribute to the synthesis of many optically active acids was that led by P. A. Levene. This group (38) not only synthesized numerous optically active alkyl-, hydroxy-, and halogen-substituted aliphatic acids and related esters, alcohols, and hydrocarbons, but they advanced a number of principles correlating the structures of these compounds with their optical rotational behavior, which may be summarized as follows.

They concluded from these investigations that the optical rotation of each molecular species may be regarded as the resultant of two major contributions. In the case of acyclic hydrocarbons of the trisubstituted methane type, the two heavier groups should furnish contributions of opposite sign. In the series represented by



an increase in the weight of R_3 should bring about an increase of the molecular rotation toward the right, whereas an increase in the weight of R_2 should have the opposite effect. When R_2 and R_3 are not simple alkyl radicals, as, for example, in



a prediction is impossible since the contribution of any group depends upon its structure and consequently it may function as a lighter or heavier group than an alkyl group of the same weight.

Thus, if $[M] = A + B$ and if A has a higher value than B , the direction of the rotation is determined by that of the contribution A . Then the values of the rotations of the consecutive members of the series, homologous with respect to A , should increase progressively. If the value of B is greater than A , the direction of rotation is determined by that of the contribution B . In this case, if a series is formed homologous to A , the changes in the rotations of the members of the homologous series should be in the direction of A , although the values may progressively diminish. Thus, if A is positive, and B is negative and of a higher value than A , the substance should rotate to the left, but as A progressively increases in weight, B remaining approximately constant, the values of the negative rotations of the successive members of the homologous series should progressively decrease, thus indicating a change toward the right.

The theoretical implications here described are illustrated in Table 28. The values of the rotations given in Table 28 for the members of the first vertical series are not the maximum values, whereas those of all other members are maximum values. A comparative analysis of the second vertical series may serve as a key to the character of each of the two contributions in all the substances listed in Table 28. The rotation of the first member is negative and that of all successive members is increasingly positive, indicating that the contribution of the heavier alkyl radical is positive, and that of the group containing the carboxyl is negative. In the first member the direction of rotation is determined by the group $-(CH_2)COOH$; in the remaining members by that of the heavier alkyl radical. Assuming then that the direction of the contribution A remains constant for all these configurationally related substances, the conclusion is reached that in all the substances enumerated in Table 28 the contribution B is levorotatory. In the substances of column 1, the value of B is higher than that of A , hence all the members rotate to the left. In column 2 the negative value of B is smaller than in column 1, so that it determines the direction of rotation of the first member only. In column 3 the value of B is higher than A , so that all members rotate to the left, but the rotations progressively change toward the right because of the increase in the dextrorotation of the contribution A . Finally, in column 4 the value of B is still higher than that of A , but not to the same extent as for the members of column 3; hence the values of rotation of the individual members are lower than those of the corresponding members of column 3 and again, the change of rotation of the individual members is progressively toward the right.

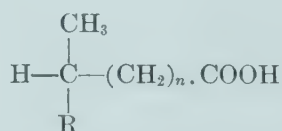
Comparing the members of any horizontal row, one observes an alter-

TABLE 28
Maximum Molecular Rotations, $[M]_D^{25}$, of Configurationally Related Methyl-Branched Alkanoic Acids

1	2	3	4	5
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{COOH} \\ \\ \text{C}_2\text{H}_5 \end{array}$ -18.0	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{COOH} \\ \\ \text{C}_3\text{H}_7 \end{array}$ -10.4	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_2\text{H}_5 \end{array}$ -13.6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_2\text{H}_5 \end{array}$ -11.1	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_2\text{H}_5 \end{array}$ -12.2
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{COOH} \\ \\ \text{C}_3\text{H}_7 \text{ (n)} \\ \text{levo} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{COOH} \\ \\ \text{C}_3\text{H}_7 \text{ (n)} \\ +3.6 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_3\text{H}_7 \text{ (n)} \\ -6.9 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_3\text{H}_7 \text{ (n)} \\ -3.7 \end{array}$	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{COOH} \\ \\ \text{C}_4\text{H}_9 \text{ (n)} \\ \text{levo} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{COOH} \\ \\ \text{C}_4\text{H}_9 \text{ (n)} \\ +6.1 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_4\text{H}_9 \text{ (n)} \\ -4.1 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_4\text{H}_9 \text{ (n)} \\ -1.7 \end{array}$	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{COOH} \\ \\ \text{C}_5\text{H}_{11} \text{ (n)} \\ \text{levo} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{COOH} \\ \\ \text{C}_5\text{H}_{11} \text{ (n)} \\ +8.1 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_5\text{H}_{11} \text{ (n)} \\ -1.9 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{C}_5\text{H}_{11} \text{ (n)} \\ -0.6 \end{array}$	

nating change in the values of the rotations of individual members. Thus, it seems as if the carboxyl group attached directly to the asymmetric carbon atom furnishes a higher negative contribution than the corresponding group of the second horizontal members. The third member furnishes a higher contribution than the second member and lower than the fourth, thus the contributions are $1 > 2 < 3 > 4$. Thus, the effect of distance upon the contribution of a polar group is to change the value only and not the sign.

Levene, Rothen, and Marker (39) reported comprehensive data on the rotary dispersion of a series of configurationally related fatty acids of the general type



where n varied from 0 to 1 and R from C_2H_5- to $\text{C}_{11}\text{H}_{21}-$. All of these acids contain an asymmetric carbon atom and are, therefore, optically active. Data pertaining to the molecular rotation of these acids are given in Table 29. These authors determined the rotatory dispersions for a number of acids of Table 29 over a wide range of wavelengths of light extending into the far ultraviolet.

TABLE 29

Maximum Molecular Rotations, $[M]_{5892.6}^{25}$, of Configurationally Related Methylalkanoic Acids without Solvent

2-Methylbutanoic	-18.0	3-Methyloctanoic	+ 8.1
Ethyl ester	-22.9	Ethyl ester	+ 4.1
2-Methylpentanoic	-21.4	4-Methylhexanoic	-13.6
Ethyl ester	-27.5	4-Methylheptanoic	- 6.9
		4-Methyloctanoic	- 4.1
2-Methylhexanoic	-24.3	4-Methylnonanoic	- 1.9
2-Methylnonanoic	-27.3	5-Methylheptanoic	-11.1
2-Methyldodecanoic	-27.5	5-Methyloctanoic	- 3.7
3-Methylpentanoic	-10.4	5-Methylnonanoic	- 1.7
Ethyl ester	-11.5	5-Methyldecanoic	- 0.6
3-Methylhexanoic	+ 3.6	6-Methyloctanoic	-12.2
Ethyl ester	+0.69		
3-Methylheptanoic	+ 6.1		

Following the work of Levene and co-workers a hiatus occurred in this field until Cason in the United States, Weitzel in Germany, the Stenhagens

in Sweden, Truter in England, Breusch in Turkey, and others undertook the synthesis of a large number of branched-chain fatty acids, many of which were optically active. The contributions of these workers (see preceding chapter) were stimulated in part by the difficulties encountered in determining the exact structures of the various physiologically active branched-chain acids that continued to be isolated from bacillus lipids, and also from the discovery of similar acids in wool fat, butter fat, mutton fat, ox perinephric fat, and various other fats.

Branched-Chain Acids. By far the greatest number of known optically active aliphatic acids possess branching alkyl chains. The number of such acids derived from natural fats has increased markedly in recent years but unfortunately in many cases their optical rotations were not reported by the workers who isolated them. The majority of synthetic branched-chain acids reported in the literature are racemic mixtures and hence optically inactive. The molecular rotations of the acids prepared by Levene and co-workers are given in Table 29; additional ones will be found in Table 6, Chapter II. Some of the better known optically active branched-chain acids isolated from natural sources are given in Table 30.

TABLE 30
Optically Active Acids from Natural Lipids

<i>Alkyl-branched</i>		
Tuberculostearic, D-(-)-10-methyloctadecanoic	$C_{19}H_{38}O_2$	$[\alpha]_D^{22} +0.08^\circ$
Phytomonic, D-(+)-11-methylnonadecanoic	$C_{20}H_{40}O_2$	$[\alpha]_D^{23} +0.05^\circ$
Phthioic, 3,13,19-trimethyltricosanoic (?)	$C_{26}H_{52}O_2$	$[\alpha]_D +12.56^\circ$
C_{27} -phthienoic, <i>trans</i> -2,4-dimethyl-13- <i>n</i> -amyl-2-eicosenoic (?)	$C_{27}H_{52}O_2$	$[\alpha]_D^{25} +19.6$
Mycoceranic, 2,4,6-trimethyloctacosanoic (?)	$C_{31}H_{62}O_2$	$[\alpha]_D -5^\circ \text{ to } -6^\circ$
<i>Epoxy and hydroxy</i>		
Vernolic, 12-13-epoxy-9-octadecenoic	$C_{18}H_{32}O_3$	$[\alpha]_D -8^\circ$
Ricinoleic, (D)-12-hydroxy-9-octadecenoic	$C_{18}H_{34}O_3$	$[\alpha]_D +6.7^\circ \text{ to } +7.8^\circ$
Hydroxynervonic, (D)-2-hydroxy-15-tetracosenoic	$C_{24}H_{46}O_3$	$[\alpha]_D^{20} +2.87^\circ$
Cerebronic, (D)-2-hydroxytetracosanoic	$C_{24}H_{48}O_3$	$[\alpha]_D +3^\circ \text{ to } +4^\circ$
Mycolic, $CH_3(CH_2)_{23}C[CH(OH)R]-CHCOOH$	$C_{88}H_{176}O_3$	$[\alpha]_D^{25} +1.8^\circ$

Hydroxy Acids. When a hydrogen of the methylene chain of a fatty acid is substituted by another atom or radical there is produced in the

molecule an asymmetric carbon atom and a plane of asymmetry. For example, if a hydroxyl group replaces a hydrogen atom in oleic acid, the resulting acid is optically active. For this reason, ricinoleic, or 12-hydroxyoleic acid, is optically active whereas oleic acid is not. Its rotation has been reported (40) to vary from $[\alpha]_D = 6.25$ to 7.5. On conversion to its *trans*-isomeride by treatment with oxides of nitrogen its rotation remains the same, both in magnitude and sign, since ricinoleic and ricinelaidic acids are geometric and not optical isomers. The esters of ricinoleic acid are also optically active. Their activities, $[\alpha]_D^{15}$, have been reported (41) to be as follows: methyl ricinoleate, 5.20; ethyl ricinoleate, 4.48; *n*-propyl ricinoleate, 4.35; isobutyl ricinoleate, 4.22.

Other optically active monohydroxy acids isolated from seed fats, waxes, or resins include convolvulinolic (11-hydroxypentadecanoic) obtained by Taverne (42) in 1894; juniperic (16-hydroxyhexadecanoic) and sabinic (12-hydroxydodecanoic) obtained by Bougault and Bourdier (43) in 1909; jalapinolic (11-hydroxyhexadecanoic) obtained by Power and Rogerson (44) in 1912; and phellonic (2-hydroxydocosanoic) obtained by Zetzsche and Sonderegger (45) in 1931. Several optically active dihydroxy acids have also been isolated from seed fats, e.g., ipurolic (3,11-dihydroxytetradecanoic) obtained by Power and Rogerson (46) in 1908 and dihydroxystearic acid obtained by Eibner and Münzing (47) in 1925. The isolation of cerebonic (12-hydroxydocosanoic) acid by Thudichum (48) in 1901 and hydroxynervonic acid by Klenk (35) in 1926 have already been noted. All of the foregoing and other related acids were discussed in the preceding chapter. King (49) isolated dihydroxystearic acid (m.p. 141° C.) from the sludge deposited on settling commercial ricinoleic acid. Polarization of this acid in warm alcohol solution gave a specific rotation of $[\alpha]_D^{50} -0.15^\circ$, but the author concluded that the observed rotation of 0.7' was probably within the limits of experimental error.

Chibnall, Piper, and Williams (50) found that phrenosinic acid obtained from the cerebroside, phrenosin, consisted of a mixture of α -hydroxy-*n*-hexacosanoic (15%) and α -hydroxy-*n*-tetracosanoic acids (85%). The purest product obtained melted at 102.3–102.6° C. and had an optical rotation in pyridine of $[\alpha]_D^{22} +3.33^\circ$. For purposes of identification with the natural acids the α -hydroxy acids of the series C₁₃ to C₁₈ were prepared, but since they represented racemates they were optically inactive. The results of Chibnall *et al.* were subsequently confirmed by Crowfoot (51).

An inseparable mixture of optically active hydroxy acids was isolated

from the lipids of the leprosy bacillus by Anderson and co-workers (52) and assigned the name leprosinic acid. This product had a specific rotation $[\alpha]_D + 4$. Several hydroxy acids have been isolated from brain cerebrosides and at least one has been isolated from the wax derived from *Mycobacterium tuberculosis*. One epoxy acid (vernolic) has been isolated from a natural lipid. The specific rotations of these acids are given in Table 30.

Chaulmoogra Acids. The most extensive homologous series of naturally occurring optically active acids are those of the group of chaulmoogra acids. Seven acids of this series are known, all consisting of an aliphatic acid having an ω -substituted cyclopentenyl ring. They owe their optical activity to the presence of one or more asymmetric carbon atoms. The specific rotations and other properties of the acids and ethyl esters of the chaulmoogra series are given in Tables 26 and 27, Chapter II.

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CHAPTER IV

X-RAY DIFFRACTION AND POLYMORPHISM

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New Orleans, Louisiana

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1. Introduction

The diamond is pure carbon, and so is graphite. But the diamond is extremely hard, transparent, a nonconductor of heat and electricity, and has a specific gravity of 3.5. Graphite, on the other hand, is very soft,

opaque, a good conductor of heat and electricity, and has a specific gravity of 2.2. This example from Klug (1) illustrates that, although the chemical and physical properties of a substance depend mainly upon its molecular structure, its crystal structure is responsible for others. Many important properties of fatty acids and of their derivatives are primarily dependent upon crystal structure, i.e., the manner in which the molecules or atoms are arranged in the crystal unit or lattice.

The present chapter is concerned with a discussion of the crystal structures of the fatty acids and their derivatives, including their crystallography, x-ray diffraction, polymorphism, and changes from one polymorphic form to another.

2. Crystallography

From the earliest times man has been fascinated by the characteristic regularity of the geometric form of crystals. Solids possessing this ordered arrangement seemed to be the exception—even rare—among the mass of material which created his environment. Modern chemistry and physics have shown, however, that most solids are crystalline and reveal, when examined with the powerful tools now available, a considerable degree of symmetry. The term amorphous solid, originally applied to the great mass of solid material which did not exhibit obvious crystal properties, must now be reserved for the very small percentage of substances which show no evidence of crystallinity even when examined with modern tools. Such amorphous solids are regarded as supercooled liquids of great viscosity and include such substances as glasses, resins, polymers, etc. These materials are frequently called glassy or vitreous, the word solid now being reserved for crystalline solids.

When a substance solidifies from its melt, from solution, or even from the gaseous phase, the peculiarities of internal structure exert strains which, if free from outside influences, are expressed in the external form of the mass. The result is the formation of a solid body, bounded by smooth surfaces, called faces, in straight edges intersecting at angles which are constant for a given substance (first law of crystallography). The resulting polyhedron is known as a crystal, meaning originally "clear ice," probably from the idea that intense cold was required for crystal formation. Dana (2) defines a crystal as a "regular polyhedral form, bounded by smooth surfaces, which is assumed by a chemical compound, under the action of its interatomic forces, when passing, under suitable conditions, from the state of a liquid or a gas to that of a solid."

There are two properties in particular by which crystalline substances can be most readily recognized and differentiated from amorphous materials. The first of these is melting point. As the temperature is raised, a point is reached at some definite temperature where the forces holding the atoms in their regular array are overcome and melting takes place. At this temperature a fixed amount of energy per unit weight is needed to overcome the crystalline forces and a definite latent heat of fusion is observed. Amorphous substances when heated do not melt at fixed temperatures but gradually soften by imperceptible degrees and become more fluid, and they exhibit no latent heat of fusion. The second characteristic property of crystals, which differentiates them from amorphous solids, is that, because they are composed of atoms or groups of atoms arranged in a regular and repeated pattern, they are not, in general, the same in nonparallel directions. Crystals are anisotropic, i.e., they exhibit properties which depend in magnitude upon the direction in which they are measured. Similar properties of amorphous materials do not vary with direction.

As illustrated in the example of the diamond and graphite, crystalline solids may exhibit polymorphism, i.e., they have the same chemical composition but different crystalline properties. Pure crystalline chemicals may also be isomorphic, i.e., they have the same crystalline properties but different chemical composition.

The idea of an underlying regular structure has always been the basis of scientific studies of crystals. This idea is suggested by the outward form and symmetry of crystalline materials and suggests the necessity to explain the regular internal arrangement of crystals, the laws governing crystal symmetry, and the regularities of the physical properties associated with crystallinity.

X-ray diffraction has been the principal modern tool used for the examination of crystals. However, early crystallographers were convinced that the regularity of form and symmetry of crystals could be accounted for by some regular arrangement of fundamental units in space. Huygens (3) in 1690 put forward the idea that a crystal was essentially a regular piling of atoms or molecules similar, on a minute scale, to a pile of shot or to the blocks of the Great Pyramid. Hooke (4) noticed the regularity of minute quartz crystals and suggested that they were built up of spheroids. Häuy (5) in 1784 demonstrated that the characteristic form of calcite, CaCO_3 , could be obtained by stacking together extremely small cleavage rhombs as the elementary unit. In the following century, mathematicians and crystallographers, utilizing the laws of symmetry and ob-

servations on the external forms of natural crystals, developed a purely geometric theory of the manner in which space might be divided by parallelehedra to account for the observed forms. They extended the theory to the representation of these units by points regularly arranged in space, the points being independent of the "building blocks" originally chosen. These points are arranged in a regular three-dimensional trellis work which embodies all the symmetry properties of the crystal. This network of points is known as the space lattice, a simple example of which is shown in Figure 1.

That there are possible 32 types of symmetry in crystals was first proved by Hessel in 1830 and rediscovered by Gadolein in 1867. A description of the nature of the symmetry for each class of crystal is provided by a

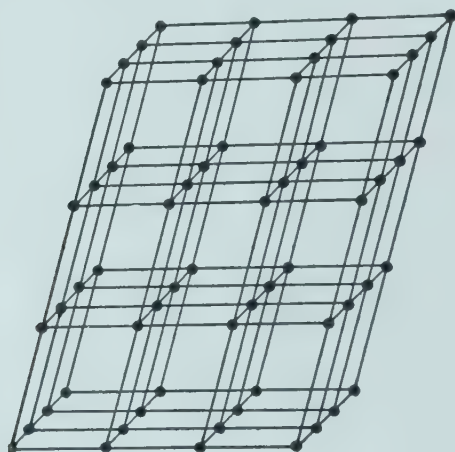


Fig. 1. A space lattice of points (17).

group of symmetry elements which is termed collectively a point group. Crystals are considered as belonging to one or another class of 32 point groups of crystal symmetry, corresponding to the 32 types of symmetry. Diagrams of these 32 classes of crystal symmetry may be found in Miers' *Minerology* (6).

By joining the points of a space lattice, a series of parallel-sided unit cells is produced, each of which is an actual crystal containing a complete unit of the crystal pattern. The whole structure is obtained by packing these cells side by side in space. The ultimate goal of crystal analysis is to establish the exact location of all atoms in the crystal in order to explain completely the crystals symmetry.

For the precise description of the almost unlimited number or atomic

arrays in crystals, there is needed a knowledge of the possible arrangement of points in space, such that the distribution as a whole possesses crystallographic symmetry. The almost simultaneous discovery of three crystallographers, Fedorov (7), Barlow (8), and Schencke (9), proved that there are 230 nonidentical space-point arrangements, designated the 230 space groups. The 32 point groups define all the possible ways of distributing points about a single point in space such that the arrangement has crystallographic symmetry. If such point groups are placed at the points of a space lattice, 65 space groups can be derived. By consideration of reflection planes with translations, which have no place in point groups but are legitimate in an infinitely extended point system, 165 additional space groups can be described. Descriptions of crystal properties in this manner is the science of crystallography. When x-rays are employed, it becomes x-ray crystallography. The geometric theory of space groups was developed many years before its practical application became possible and was ready in a complete framework within which x-ray results could be incorporated.

3. X-Ray Diffraction

(a) *Introduction*

X-radiation includes that portion of the electromagnetic spectrum below the far ultraviolet, i.e., from about 10 to 0.1 Å. Consequently, a discussion of the applications of x-ray spectroscopy to fatty-acid chemistry may be considered as pertaining essentially to spectral properties. The applications of emission (fluorescence) and absorption of x-rays for the purpose of detection and quantitative determination of specific substances are discussed in Chapter V.

A fundamental discovery by Laue has made investigations involving the diffraction of x-rays considerably more important to the elucidation of crystal properties than are the spectral properties of a substance. A simple consideration of the atomic weight of any element, the average density of solid matter, and Avogadro's number shows that the distance between atoms in a solid must be about 2×10^{-8} cm. on the average. Thus, if radiation with a wavelength in the range of magnitude of 1 to 2 Å. is passed through a crystal, diffraction effects should occur much as an ordinary ruled grating causes diffraction of radiation in the visible range.

Laue was the first to announce this conclusion, namely, that crystals should act toward x-rays much as a ruled grating acts toward ordinary light. Several experimental investigations were immediately initiated to

study the possible diffraction of x-rays. Foremost among these were the investigations of Bragg (10) on the diffraction of monochromatic x-rays by a single crystal. In Figure 2, monochromatic x-rays defined by the lead slits, S_1 , S_2 , S_3 , fall on the crystal at C , at grazing incidence. In general, the reflected wave-trains from successive planes will be out of phase with each other and will interfere so that no reflection will result. However, if the path distance of the wave in going from plane to plane is an exact multiple of the wavelength, λ , of the monochromatic x-rays, all the reflected waves will be in phase and the train as a whole will be reflected by the crystal at some point along P , the photographic plate. This will occur when, and only when:

$$\sin \theta = n\lambda/2d$$

where θ is the angle between the atomic plane and both the incident and reflected beams; d is the interplanar spacing between successive atomic

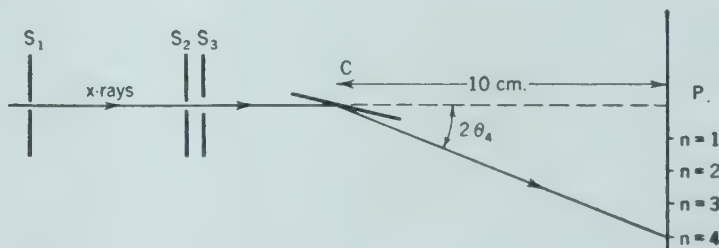


Fig. 2. Schematic representation of x-ray diffraction method.

planes in the crystal; and n is an integer, the so-called "order of the reflectance." This relation is known as Bragg's law.

If the crystal, C , is stationary, only a few reflections will be recorded. However, if the crystal is mounted with a face on the axis of a rotating table, the reflected waves will be in phase for different "orders of reflection" and a series of diffraction lines will be photographed. If d is determined for a specific crystal by independent means, λ , the wavelength of the monochromatic x-ray beam can be measured.

The discovery by Laue received considerable attention as it clearly showed that x-rays were waves, i.e., they could be diffracted like ordinary light waves. Attention was given to the method for the determination of the wavelength of x-rays. Structural determinations of the alkali halides, NaCl and KCl, accomplished by Bragg (11), established their interplanar spacings d . Wavelength determinations could be made by using these materials as crystals to diffract the x-rays. Experimental work to verify

the discovery of Laue was carried out mainly by Bragg and by Barkala. The importance of the work is emphasized by the fact that all three of these scientists received Nobel Prizes for their work, Laue in 1914, Bragg in 1915, and Barkala in 1917.

As the dual wave-corpuseular nature of x-rays (and other electromagnetic radiation) became well established, Bragg's law became useful for the determination of d , the interplanar spacing of crystals, by making measurements with monochromatic x-rays of known wavelength. The discovery of Laue that a crystal will cause diffraction of x-rays has led to the science of x-ray crystallography. X-rays are now one of the most important tools for the study of crystal properties.

When fast-moving electrons impinge on matter, they may strike and displace tightly bound electrons deep in the atom near the nucleus. The atoms are thus ionized and when electrons from shells farther out from the nucleus fall into the vacant spaces thus created, there will be a resulting emission of x-rays characteristic of the atom involved. These characteristic x-ray spectra are exactly analogous to the characteristic spectral lines of electronic spectra. (See Chapter V). In electronic spectra, transitions between outer orbits of the atoms, i.e., valence electrons, give rise to characteristic atomic lines in accordance with the quantum equation:

$$\Delta E = h\nu$$

where ΔE is the difference in energy between the two orbits and the energy of the emitted radiation. The quantum equation merely states that this energy difference must be some integral value, h , (Planck's universal constant) of the frequency of the emitted radiation, ν . The emitted radiation will have a frequency dependent upon ΔE , which in turn is dependent upon the orbits (or energy levels) within the atom. The exact frequency is, thus, dependent upon the structure of the characteristic atom.

In x-ray spectra, transitions occur and follow exactly these same laws. But, in x-ray spectra, the transitions are between the most inner orbits of the kernel of the atom. When an electron is ejected from the most inner orbit, the K shell, an electron may fall from the next shell, the L level, causing an x-ray line characteristic of the particular atom. This transition between the L and K shells is called a K_α line. If the vacancy in the K shell is filled by an electron from the next, the M shell, the resulting line is known as a K_β line. K lines are those which originate from vacancies in the K shell. Similarly, x-ray lines originating from the L shell are called L lines; from the M or N shells, M or N lines; etc. As the L shell,

like all shells outside the K level, possesses several energy levels, the electron falling from this level to fill a vacancy in the K shell may fall from more than one sublevel in the L shell, giving rise to K_{α_1} , K_{α_2} , etc., x-ray lines. Similarly, transitions between the M and K levels may give rise to K_{β_1} , K_{β_2} , etc., and transitions between the M and L shells account for L_{α_1} , L_{α_2} , etc.

In general, for diffraction studies the target material, upon which the fast-moving electrons impinge and give rise to the x-ray beam, is usually copper, molybdenum, nickel, silver, cobalt, iron, or chromium. Elements with lower atomic numbers are too readily absorbed, while those with higher atomic numbers have too intense a continuous radiation which tends to mask the characteristic K, L, or in some applications, the M and N lines.

(b) Techniques of X-Ray Diffraction Measurements

A complete description of the instrumentation and experimental procedures for obtaining x-ray diffraction data is beyond the scope of this discussion. X-ray measurements required for investigations of fatty acids, esters, glycerides, and other derivatives are similar to those used in applications in other fields and are adequately described in considerable detail in several excellent texts and reference books (1,12-17). Details of individual procedures are also obtainable from instrument makers' brochures and instruction booklets which list target materials, camera arrangements, etc., recommended for specific measurements.

1. The Laue Method. The experimental arrangement first used by Laue, to demonstrate that crystals would diffract x-rays in a manner analogous to the diffraction of ordinary visible radiation by a diffraction grating, is very simple. It is the only method now in use which employs a polychromatic x-ray beam. A single crystal is placed in front of a pinhole. The polychromatic x-ray beam, usually from a tungsten target, is collimated to nearly a parallel beam. The designs of the collimator and the pinhole are important; the longer the collimator, the more parallel the x-ray beam, and the smaller the pinhole; the sharper will be the Laue spots on the photographic plate or film. However, the time of exposure increases with the decreased diameter of the pinhole and the increased length of the collimator.

The Laue spot is a reflected image of the pencil of x-rays striking the crystal. The only variables in the Bragg equation, with such an arrangement, are the wavelength, λ , and the order of reflection, n . If λ were fixed,

only a very few sets of planes would be in a favorable position to meet the requirements of the Bragg equation and only a few reflections would appear as Laue spots on the photograph. But in the whole range of wavelengths in the continuous x-ray spectrum, there will be some of value λ which will satisfy the Bragg condition no matter what may be the orientation of the lattice planes. In other words, each set of planes picks out from the heterogeneous beam one particular wavelength which can be reflected in accordance with the Bragg law.

A typical Laue photograph consists of a series of spots whose loci are symmetrically disposed about the point where the primary central x-ray beam would strike the film. Usually the primary beam is absorbed by a lead stop to avoid over-exposure of the central portion of the film. Each spot is the result of a reflection of a particular wavelength of x-ray at a definite diffraction angle from a certain set of planes. The technique yields only a limited amount of information, but it is an easy method of obtaining qualitative data on the reflections from a large number of crystal planes.

2. The Bragg Method. This method is essentially described in the discussion of the derivation of the Bragg equation. It uses monochromatic x-rays and a slit diaphragm, or a pinhole, if the crystal is very small. The method involves only a reflection from a single set of planes. For any additional measurements, successive resettings of the crystal are required so that the planar distances for each of the various sets of planes that have a common zone axis are ascertained. The method provides the most complete data for calculating spacings for the sets of planes and computing the size of the unit crystal cell. The difficulty is that the continual resettings of the crystal are both tedious and time-consuming.

3. The Rotation Method. The patterns obtained with the polychromatic x-ray beam are difficult to interpret and monochromatic x-rays provide only diffraction from a single set of planes on a single photograph; hence it is simpler and easier to use the rotation method developed by Polanyi *et al.* (18). The method has been completely described by Bernal (19). The crystal is mounted with a principal crystallographic axis perpendicular or vertical to the plane and it is then rotated about this direction as axis. The rotation may be continuous or may take the form of an oscillation. Three such photographs are usually taken about the principle axis and these give almost complete information. Clark has called this method the most powerful method of crystal analysis (14).

4. The Powder Method of Debye-Scherrer and of Hull. The powder method was described by Debye and Scherrer in 1916 (20) and inde-

pendently by Hull in 1917 (21). A monochromatic x-ray beam is used and the sample in the form of a crystalline powder contained in a small tube or in the form of a thread or a ribbon is fixed in its path. In the Debye-Scherrer method, a pinhole diaphragm is used while Hull uses an x-ray beam defined by a slit. A narrow film is bent cylindrically with the specimen at the center of curvature. The pattern is obtained as a series of lines, each line corresponding to a set of planes. By measurements of the displacements of these lines on the film from the position of the central beam (the angle of deviation) the interplanar spacings may be calculated.

The Debye-Scherrer-Hull method has several advantages: (a) it is applicable to compounds which can be obtained only in minute crystals; (b) there is practically complete coverage of all the reflection produced by the specimen in a single exposure; (c) the data are obtained relatively rapidly; and (d) the apparatus and the technique required are relatively simple. The method is particularly useful for studies of allotropy, for qualitative and quantitative analyses, and for the determination of the purity of substances. It is the method of the analytical chemist as distinguished from that of the crystallographer. It is the procedure used in obtaining most of the data in the library of x-ray diffraction cards available from the American Society of Testing Materials for the identification of pure crystals by means of their x-ray diffraction patterns.

5. The "Flat Film" Method. A monochromatic x-ray beam defined by a pinhole diaphragm is also employed in this method. The specimen may be a crystalline powder, fiber, or a fluid (often a material crystallized from solution or melt on a microscope cover glass). The axis of the specimen is placed at right angles to the x-ray beam; ordinarily from 2 to 20 cm. beyond the specimen is placed a flat film, also at right angles to the central x-ray beam. In studies of large spacings, longer specimen-to-film distances are used. The pattern is obtained for a random aggregate and consists of a series of concentric rings. When orientation exists in the structure of the specimen, it will show in the diffraction pattern as increased densities or spots on the rings. The rings may also become flattened and crescents or sickles may appear on the film. From the diameter of the rings, the interplanar spacings are calculated; and from the intensity and position of the spots, the degree and direction of orientation of the planes are found. Klug and Alexander (1) rank this method next in utility to the Debye-Scherrer-Hull technique for investigation of polycrystalline materials.

The foregoing brief descriptions pertain only to the simpler techniques employed to investigate the crystals properties of fatty acids and their

derivatives. More complicated apparatus, such as cameras with moving films, the Weissenberg goniometer, the Schiebold-Sauter or the Dejong-Bowman camera arrangements, or the Buerger-Supper precession camera, make it possible to obtain essentially all the information required on a single photograph. The use of these methods, especially the interpretation of the results obtained by their application, requires specialized training in crystallography. This is particularly true in single crystal analysis where it is desired to obtain a complete crystallographic description of a given substance.

4. Early X-Ray Investigations

The earliest investigations of the x-ray diffraction of long-chain fatty acids and related compounds appeared about the middle of the 1920's. These contributions were made, for the most part, by two groups of British workers, namely, Müller, Shearer, and co-workers, and Piper, Francis, and their colleagues who contributed some thirty papers on this subject between 1923 and 1938.

Müller, Shearer, and co-workers melted samples on glass plates where, as they crystallized in flakes, they oriented themselves parallel to the glass surface and acted as single crystals. Very satisfactory diffraction patterns were obtained when the crystal holder was oscillated. In later investigations some samples were mounted on strips of mica, the well-known diffraction lines of which afford an automatic plate or film calibration. Figure 3 illustrates a typical diffraction pattern of a long-chain



Fig. 3. Typical diffraction pattern from "pressed" layer of long-chain hydrocarbon. Arrows indicate lines from mica.

hydrocarbon with the mica calibration lines. By means of this relatively simple technique, data were obtained on the x-ray diffraction of long-chain saturated acids (22), esters (23), unsaturated acids (24), ketones (25), and for purposes of comparison, long-chain hydrocarbons (26). Interpretation of these data introduced several basic principles upon which were rapidly built the now-accepted techniques of investigating

long-chain fatty acids and their derivatives by x-ray diffraction. The more important conclusions derived from these and other early experiments include the following:

1. X-ray diffraction patterns of long-chain compounds reveal the existence of two (sometimes more, but occasionally only one) small (short) spacings which have about the same values for all substances in a homologous series, and a third spacing of greater length which increases proportionally to the number of CH_2 groups in the particular compound. These spacings suggest that the unit cell is a long prism which has the same cross section for all substances in a series. The length of this prism is indicated by the long spacing (22) of the x-ray diffraction pattern. The first of these spacings was called small or side spacings until Malkin (27) introduced short spacing as a more appropriate term. The spacing, indicating the length of the prism, is designated *long spacing*, and is a measure of the length of the carbon chain. It is the most characteristic feature of the diffraction pattern of long-chain compounds.

2. Addition of the diameters of the carbon and oxygen atoms in a straight line would give a maximum distance for an 18-carbon acid of about 30 Å., but the measured long spacing of stearic acid is 38.7 Å., therefore, the unit cell must contain more than one molecule. Half of this measured distance, however, would be considerably less than the theoretical length. It was concluded, therefore, that the unit cell must consist of two molecules between parallel planes and that the atoms in these chains must be arranged in a zigzag pattern (22).

From crystallographic measurements with a single crystal of stearic acid (obtained by crystallization from solvent) Müller (28) showed that this compound crystallizes in the monoclinic prismatic system of the space group C_{2h} . The axial dimensions of the elementary parallelepiped are; $a = 5.546$; $b = 7.381$; $c = 48.84$ Å. The b -axis is perpendicular to the plane ac but the c -axis is inclined so as to produce the angle β between the a - and c -axis of $63^\circ 38'$. The density is slightly more than 1.05; this gives four molecules to the unit cell. The rectangular base of the cell has the dimension 7.4×5.6 or an area of 41.4 Å.^2 . In such a cell the arrangement of the molecules is such that their ends are found at the corners and in the center of this rectangle. The area is a measure of the space occupied by the base of two molecules so that each molecule stands on a base of average 20.7 Å.^2 (29).

A diagrammatic representation of the unit cell of a stearic-acid crystal is shown in Figure 4 (30). What is measured by the x-ray spectrometer from the melted sample (22) is the perpendicular distance between two

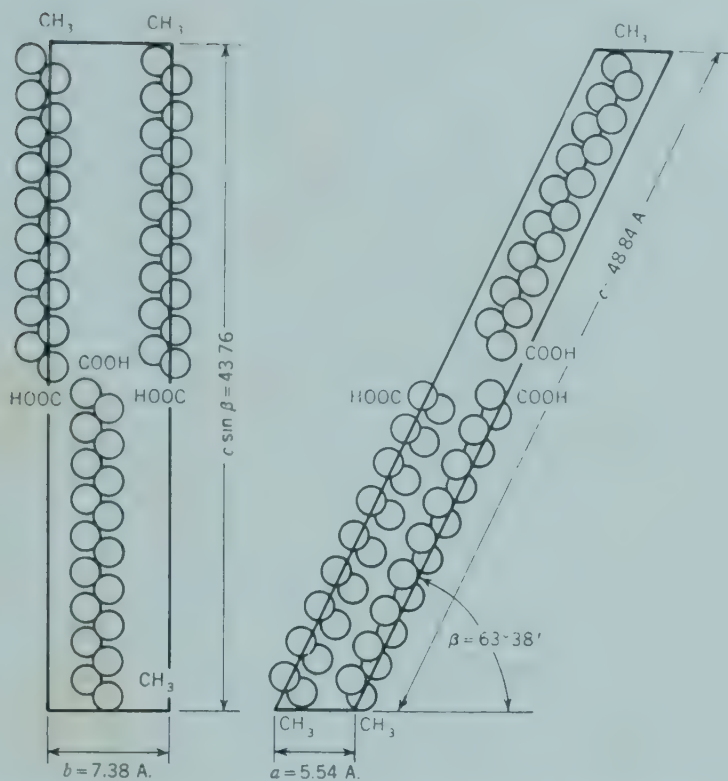


Fig. 4. Diagrammatic representation of the unit cell of a stearic acid crystal (30).

planes of the crystal which are identical with each other. In Figure 4 this distance, $c \sin \beta$ equals 43.76 Å. This value, 43.76 Å., is the measured long spacing of the B-form of stearic acid. It does not follow that the direction of the length of the molecule is perpendicular to the cleavage plane. However, x-ray patterns show that for several homologous series there is a uniform increase in the measured long spacing per CH_2 group. When the long spacings are plotted against the number of carbon atoms, they fall on a straight line. Hence, it is necessary to conclude that for any one series the molecules are all inclined at the same angle to this plane.

3. If it is assumed that the distance between carbon atoms is about 1.5 Å. from the measured long spacing of a specific compound of known carbon length, the angle of the zigzag arrangement can be calculated as $109^\circ 30'$. This is almost exactly the angle which the normals from the center of the faces of a tetrahedron make with each other (23). The atoms are, therefore, arranged in a zigzag chain with an angle corresponding to the tetrahedral carbon angle, $109^\circ 30'$, Figure 5.

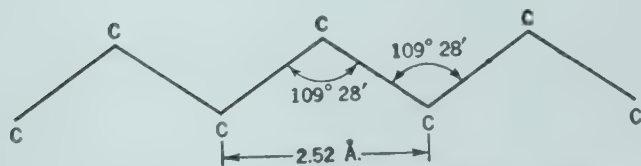


Fig. 5. Diagrammatic representation of the zigzag carbon chain of aliphatic acids.

The hydrocarbon *n*-nonacosane has been shown from complete crystallographic analysis to have a unit cell similar to that of stearic acid but with the *c*-axis perpendicular to the *bc* plane, rather than tilted. The *c*-axis in this compound is 77.2 Å., from which it can be readily calculated that the distance between alternate carbon atoms, i.e., twice the distance between carbon atoms, is 2.54 Å. From the diagram, Figure 5, the distance between alternate carbon atoms can be calculated as 2.52 Å. The excellent agreement between this value and that obtained from experimental data on *n*-nonacosane is strong confirmation for the zigzag arrangement of the carbon atoms in long-chain compounds.

If the uniform increase per CH_2 group for a specific homologous series is evaluated, and if the zigzag arrangement with the angle $109^\circ 30'$ is accepted, the long spacing of an individual member can be calculated. Comparison of this value with the measured long spacing of an individual member of the series yields data from which it may be determined whether the particular series crystallizes with one, two, or more molecules between successive layers. The long spacing increase per CH_2 for the aliphatic saturated hydrocarbon series is found to be 1.3 Å. Eicosane, $\text{C}_{20}\text{H}_{42}$, has a long spacing of 28.0 Å.; $20 \times 1.3 = 26$ Å., indicating one molecule between successive layers.

It is apparent from Figure 5 that the average distance between carbon atoms is 1.26 Å. Hence, if the uniform increase in measured long spacing is about this value, then the individual members of the homologous series crystallize with a single molecule between identical plants; if it is considerably larger, e.g., 2.0 Å., as it is for the saturated fatty acids, they crystallize with two molecules between layers, etc. By this approach it has been found that the saturated hydrocarbons crystallize with a single molecule between layers; saturated fatty acids with two molecules; esters with one; all ketones, except methyl ketones, with one; methyl ketones with two; dicarboxylic acids with an even number of carbon atoms with one; dicarboxylic acids with an odd number of carbon atoms with two; hydrocarbons with benzene rings with two; etc.

From these observations Shearer (29) concluded "if the molecule has

at one end a group which is active chemically, e.g., COOH , then the double layer will be found; if both ends are inactive, as in the hydrocarbons, only a single layer will occur. As it appears to be the active groups which result in the formation of the double layer, the natural conclusion is that the two layers are oppositely oriented, the active groups of the bottom layer being directed toward the active groups of the upper layer." In the case of ketones the methyl COCH_3 group is chemically active like the COOH of the acids and these compounds crystallize with two molecules between successive layers, while all other ketones have only inactive groups and crystallize with one molecule between layers. Long-chain hydrocarbons with attached benzene rings appear to have two molecules between layers, indicating that the benzene ring is active, while all the esters have inactive groups and crystallize with one molecule between layers.

4. Once the number of molecules between successive layers is established, the differences between measured long spacings and the distances calculated on the assumption of the zigzag chain with the tetrahedral angles of Figure 5 and from the known carbon content of the chain can be used to calculate the inclination or tilt, i.e., the value of the β -angle. Thus, from Figure 2, if β is the angle of tilt then $\sin \beta = \text{long spacing when tilted} / \text{long spacing when perpendicular}$ (e.g., of the corresponding hydrocarbon); or $\sin \beta = \text{the increment per } \text{CH}_2 \text{ when tilted} / \text{the increment when perpendicular}$ (2.54).

5. Variation in the angle of tilt is the probable explanation for change in the increment in spacing per CH_2 from one series to another rather than any intrinsic change in the nature of the chain itself (29). However, members of a homologous series may exhibit different β angles and even the same substance sometimes has more than one stable arrangement, probably caused by a change in the tilt of the molecules from one stable position to another. Piper *et al.* (31,32) have shown that odd-number paraffins of 11 or more carbon atoms normally crystallize with the chain axis vertical to the 001 planes. In this case the planar spacing is a direct measurement of the length of the molecule. Even-number paraffins of 18 or more atoms crystallize in this modification at temperatures near the melting point. Even-number paraffins up to 24 atoms, at normal temperatures, crystallize with the chain axis inclined at a constant angle to the planes, the B-modification. Odd-number chains of 9 or less also adopt this modification. Paraffins having 26 or more carbon atoms crystallize stably in a third or C-modification, characterized by a larger angle of tilt, and, hence, still shorter spacings.

The saturated aliphatic acids exhibit various modifications with different angles of tilt. Acids with an even number of carbon atoms exhibit a vertical chain and two modifications with different degrees of tilt. Acids with an odd number of carbon atoms are found to have four different modifications, a vertical chain and three degrees of tilt. Similar differences have been recorded for alcohols, esters, salts, etc. A more detailed description of these modifications will be found in a later section on polymorphism. The point being emphasized here is that degree of tilt, the β -angle, (Figure 4) is undoubtedly accountable for the variations in long spacings.

6. Tilt has also been shown to be responsible for the alternation of properties in some homologous series. If the values of the x-ray spacing for the same polymorphic modifications of the various homologous series of long-chain aliphatic compounds are plotted against the number of carbon atoms in the chain, a series of straight lines is obtained, as shown in Figures 6 and 7 which are reproduced from the work of Francis *et al.* (33), and of Piper (34). This linearity in the relationship between the number of carbon atoms and spacing values contrasts with the curvilinear relationship or alternation exhibited by other properties of these compounds. As early as 1923, Müller (22) noted the alternation of intensities of the different orders of reflection, the first and third very strong, the second and fourth weak, the fifth moderately strong. Phillips and Mumford (35) observed a similar alternation of melting points of the B-forms of the ethyl esters of the saturated acids of odd and even number of carbon atoms. Similar alternation between odd and even carbon content members have been observed for freezing points, melting points, heats of crystallization, etc., of several homologous series of long-chain compounds, including paraffins, acids, esters, dibasic acids, etc.

Müller (36) attempted to account for the alternation in the properties of odd- and even-numbered chain compounds on the basis of the zigzag arrangement of the carbons in the long-chain compounds. In the even-numbered chain the end groups are parallel while in the odd-numbered chains they are not. Thus, in dibasic acids the repeating unit will be one molecule in the even-numbered homologs and two molecules in the odd-numbered members. This calculation was verified by the x-ray diffraction on dibasic acids by Caspari (37). The same explanation can account for the differences in the behavior of the β -angle in compounds containing odd and even numbers of carbon atoms, and, according to Müller (36), it is quite compatible with the observed differences in melting points of homologous members having odd and even numbers of carbon atoms.

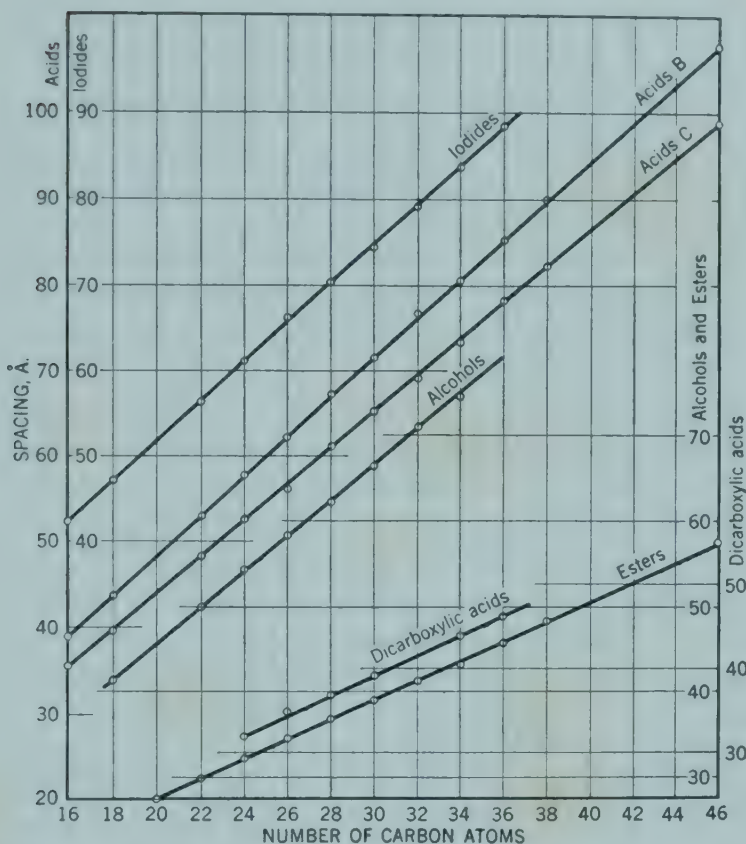


Fig. 6. Variation in spacing values as a function of the number of carbon atoms in long-chain aliphatic compounds (33).

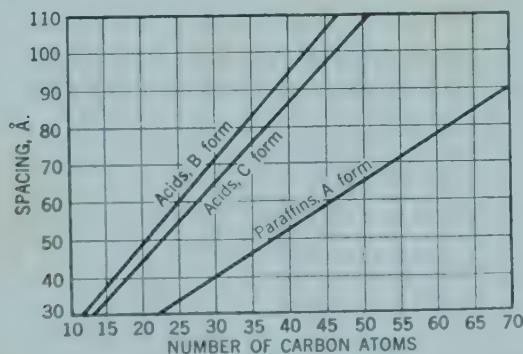


Fig. 7. Variation in spacing values as a function of the number of carbon atoms in the normal paraffins and the two forms of fatty acids (34).

Malkin (38,39) attributed the alternation in properties of long-chain compounds to tilt of the zigzag chains. He contended that Müller's

explanation of the alternation of properties presented certain difficulties because it implied that alternation occurs in all long-chain compounds, whereas the normal paraffins, methyl ketones, primary alcohols, and ethyl esters have been shown to exhibit no alternation of properties. In these compounds the crystal spacings decrease regularly with the increasing order of reflection. Malkin also pointed out that experimentally all nonalternating series possess vertical chains, whereas alternating series possess tilted chains. He demonstrated diagrammatically how Müller's theory could be extended to account for this fact by showing that the alternation of properties will occur only if the zigzag chains are tilted. It is now generally accepted that alternation of properties between odd and even members of homologous series can be accounted for by the angle of tilt.

7. For those crystals, in which there is a single molecule between successive reflecting planes, the lines of the successive orders of reflection decrease in intensity with increasing order, following what is called a normal decline. For crystals with double molecules between successive layers, there is an alternation superimposed on the normal decline, strong odd and weak even orders appearing in the first 8 or 9 lines. If the active group responsible for the double molecule contains a very heavy atom, the alternation tends to disappear and the photographs resemble more closely those of single layers, but, nevertheless the measured spacing corresponds to the length of two molecules (34).

Shearer (40) showed that with certain simple assumptions the intensity distributions can be calculated and the results compared with these experimental observations. The intensity distribution will depend upon the distribution of scattering material between the successive planes. This distribution will be uniform along a chain of uninterrupted CH_2 groups and will be unaffected by a terminal CH_3 because of the small mass of the hydrogen atom. In the saturated hydrocarbons, therefore, the distribution will be uniformly diminishing with successive orders of reflection. This assumption is verified by the observed data on several saturated straight-chain hydrocarbons.

If the terminal group is one such as the carboxyl of the fatty acids then, at this point, the scattering power will be greater than the average scattering power of the chain. In the case of esters and ketones, the ketonic oxygen attached to one of the carbons of the chain will produce at this point an increase in scattering. If a crystal has two molecules end-to-end in opposite directions between successive planes, as in the saturated fatty acids, the even order of reflection will disappear and the odd orders will

diminish in intensity in the same manner as in the hydrocarbon series. This distribution pattern is experimentally observed in the saturated fatty acids and alcohols and is attributed to the fact that the excess of scattering matter at the one end of the molecule is exactly balanced by the deficit at the other. A ketone with the carbonyl in the exact center of the long chain would behave the same as two molecules with their active groups head-to-head. The distribution would be the same as that for the fatty acids and alcohols containing two molecules between successive planes, although x-ray measurements show only one molecule for these compounds. Shearer (40) has shown that the distribution pattern for other ketones will depend upon the location of the carbonyl group; if it is one-third the distance along the chain, the third, sixth, ninth, etc., orders of reflection will disappear. Or, in general, if on the n th carbon atom, the n th, $2n$ th, $3n$ th, etc., order will disappear, and there will be a corresponding maxima of intensity at the $n/2$, $3n/2$, $5n/2$, etc., order. Shearer compared calculated intensity distributions for several compounds with the experimentally observed values and found that they were in reasonably good agreement. From a chemical point of view, the conclusions are important because they suggest a means of determining the position of the carbonyl group in a long chain.

Wilson and Ott (40a) suggested refinements in the method of Shearer and illustrated them with applications to a series of n -aliphatic alcohols. They concluded, "It should be possible to extend the theory, here presented, to the calculation of intensities of reflection for all the long-chain compounds, although many of the others offer complications which are not present in the case of the alcohols, such as tilt, double-bonded oxygen, etc. However, if the proper assumptions are made it should be possible to extend this or a similar calculation to all cases."

8. While it is well established that the angle of tilt, β , accounts for polymorphism, Malkin (41) has shown that different crystal modifications can occur without change in tilt and without involving a corresponding change in length of the long spacing. Phillips and Mumford (42) claimed that their results showed definitely that the alcohols above C_{14} with an odd number of carbon atoms exist in a tilted β -form and that Malkin's conclusions (43), which indicated that they had a vertical chain, were based on a misinterpretation of x-ray measurements. This was refuted by Malkin (41) who claimed that Phillips and Mumford assumed a tilted β -form without the benefit of x-ray measurements; that his (Malkin's) x-ray diffraction results, which showed the β -form to have vertical chains and the same long spacings as the α -form, have been confirmed by Wil-

son and Ott (44) and by Piper *et al.* (45). The α - to β -transition, it was claimed, is not due to change in tilt and does not involve change in length of long spacing. It arises from a change from a vertical rotating form (evidenced by only the one 4.2 Å. side spacing found for the α -form) to a vertical nonrotating form (evidenced by two side spacings at 3.7 and 4.2 Å. for the β -form.) The concept of uniaxial rotation was used to explain why the esters of palmitic and stearic acids readily assume the β -form, with shorter spacings and tilted chains, and why those of margaric acid more readily assume the α -form (longest spacing and vertical chain) (46). Molecular rotation in crystals was also used to explain the fact that the α -forms give only one side spacing of 4.2 Å., while the β -forms give the two side spacings (3.7 and 4.2 Å.) usually associated with long-chain compounds.

It should be noted that all of the data used in arriving at the above conclusions can be obtained from the powder pattern-type methods of x-ray measurements. The more elaborate methods of complete crystallographic analysis are not required. For any homologous series, linear relationships exist between the spacings and the number of carbon atoms in the chain. It is obvious that the spacing of a homologous series of compounds, once measured, will serve as a means of chemical identification. An observation of the intensities of the successive orders of reflection will enable a determination to be made, with reasonable accuracy, of the position of an active group. Robinson (47) reported the identification by Shearer of four keto acids submitted to him as unknown long-chain keto acids. From x-ray diffraction measurements of the simple powder-pattern type, Shearer was able to report the carbon chain lengths as 16, 18, 19, and 22 and, by means of intensity patterns of the respective orders of reflection, to place the position within one carbon atom of its correct position, of each of the carbonyl groups along its respective hydrocarbon chain.

The primary interest of the fatty-acid chemist in x-ray diffraction is in its application to the solution of some specific problem, which, however, presupposes that adequate data are available for this purpose. Much of the following discussion will, therefore, be devoted to the accumulation of the required data and their application to problems encountered in the chemistry of the fatty acids.

Müller and his co-workers repeatedly emphasized that the chain lengths of unidentified pure compounds could be determined from x-ray long spacings of known compounds. Piper and his colleagues investigated x-ray diffraction primarily as an aid in their attempts to identify the fatty acids and waxes isolated from natural products, as, for example, the constituents

of wheat wax (48). Shearer also emphasized the importance of x-ray crystal analysis to problems of chemistry (49,50,51). In the following discussion emphasis is likewise placed on the application of x-ray diffraction data to the solution of practical problems.

The discovery that most long-chain compounds exist in more than one modification has complicated the application of x-ray diffraction to chemical analysis. Ferguson and Lutton (52), in a review of the polymorphism of glycerides, pointed out that in a strict sense it is not the crystal properties of a specific compound that must be dealt with but rather those of a particular polymorphic form of the compound. It is necessary, in applying x-ray diffraction data to problems of identification, to know what crystal modification is being dealt with, otherwise unique identification is not possible. For example, the long spacings for the B-form of tridecanoic acid and for the C-form of myristic acid are identical, namely, 31.6 Å. However, the melting points of two such compounds are considerably different, hence a combination of melting point and x-ray diffraction data provides important evidence as to the chemical identity of a compound. The following discussion of the crystal properties includes reference to certain intimately related thermal properties.

5. Polymorphism

(a) Introduction

In 1925, Müller and Saville (26) observed that the hydrocarbons, octadecane ($C_{18}H_{38}$) and eicosane ($C_{20}H_{42}$), showed two sets of long spacings, one at room temperature and the other at somewhat higher temperatures. The two spacings differed by 6–7%, indicative of more than one crystal form. Saville and Shearer (25) reported two long spacings (33.6 and 30.8 Å.) for hexyl *n*-heptadecyl ketone. Piper *et al.* (53) modified the technique of Müller (22) by pressing long-chain fatty acids on a glass plate with only sufficient force to cause the flakes to adhere with the minimum breakage. X-ray photographs revealed two sets of lines, one identical to those obtained by Müller (22) and the other with somewhat greater long spacings. Patterns obtained with melted samples prepared by Müller's technique exhibited only the shorter long spacing discovered by him. In 1930, Piper and Malkin (54) reviewed the then available evidence for the existing of more than one modification of long-chain normal paraffins. Following these earliest investigations it was soon established that most long-chain compounds can crystallize in

more than one modification and that polymorphism among these compounds is a rule rather than an exception.

Polymorphic forms are solid phases of the same chemical composition, differing among themselves in crystalline form, free energy, and other physical and chemical properties, but yielding identical liquid or gaseous phases upon fusion or evaporation. This definition differentiates polymorphism from isomerism in which different solid phases or modifications have the same composition but maintain these differences in the liquid or gaseous state. In terms of the phase rule, every polymorphic form exists as a separate phase, and the number of solid phases for a single component is, therefore, the number of existent polymorphic forms; whereas any system of isomers is a two-component or multicomponent system, since the phases cannot have their composition expressed by less than two terms.

It should, however, be mentioned that these definitions apply to equilibrium conditions and do not exclude the possibility of a metastable crystalline form of a compound melting to form a metastable liquid phase. This phenomenon is well known among organic compounds which melt (metastably) and resolidify as the temperature is raised to that corresponding to a more stable or higher melting form. Also it should be noted that in some cases inversion may be difficult to accomplish experimentally.

Two types of polymorphism are recognized, namely, *enantiotropic* and *monotropic*. In the case of *enantiotropism* the different forms possess vapor pressure curves which approach each other with change in temperature and intersect at a point called the *transition point*, at which point the vapor pressures of the two forms are identical. At such a transition temperature, and only there, are both solid phases stable, and at this point an equilibrium exists between them such that the addition of heat will effect a transformation into the form stable at higher temperatures without, however, raising the temperature (isothermal transition) until the other form has disappeared, since the change occurs at an invariant or *triple point*. Abstraction of heat brings about the reverse change, also at constant temperature. This form of polymorphism is completely reversible in the solid state.

In the second type of polymorphism, namely, *monotropism*, the vapor pressure curves of the two forms do not meet and such forms lack a transition point. Under conditions where both forms can exist, the one form is always stable and the other metastable. The metastable form always has the higher vapor pressure and will, therefore, change into the

stable form by some process such as distillation. This form of polymorphism is not reversible in the solid state.

The occurrence of polymorphism is commonly observed in long-chain aliphatic compounds, and is generally the rule rather than the exception among the long-chain fatty acids, esters, glycerides, alcohols, hydrocarbons, etc. Polymorphism is particularly important in the fat and oil industry because the consistency of many products, such as lard, butter, shortening, oleomargarine, etc., is dependent on the particular polymorphic modifications that are induced in these products during processing and use. The particular polymorphic form which is assumed when long-chain aliphatic compounds crystallize depends on a variety of factors, particularly the purity of the compound, the solvent from which it crystallizes, the presence or absence of particular crystalline nuclei, temperature, rate of cooling, and degree of supercooling. Each polymorphic form is characterized by various properties, such as melting point, resolidification point, heat of crystallization, specific volume, x-ray spacing, etc., which distinguish it from any other form of the same compound. Certain forms are readily distinguishable by microscopic examination or even by visual inspection. Pure long-chain hydrocarbons are often observed as dense, opaque crystals, or again as transparent crystals resembling clear ice, corresponding to each of two different polymorphic modifications. Both enantiotropism (reversible polymorphism) and monotropism (irreversible polymorphism) are exhibited by derivatives of the fatty acids, whereas the acids themselves exhibit only monotropism.

(b) Polymorphism of Long-Chain Fatty Acids

Piper *et al.* (53) found that the saturated fatty acids gave x-ray photographs which showed that each acid can exist in at least two forms. The spacings reported by Müller (22) from samples melted on glass plates were called the C-spacings. If the crystals were pressed on the glass plate, the photographs exhibited two sets of lines, one identical with those discovered by Müller and the other with greater long spacings (and consequently a larger β -angle of tilt) called B-spacings. In addition, measurements on stearic and palmitic acids revealed a third still longer spacing, called the A-spacing. The B- and C-spacings are both tilted forms, and the A-spacing is vertical. Piper (55) reported a fourth crystal modification found only for acids with an odd number of carbon atoms, which he called the D'-spacing. He used the symbols the A', B', C' and D' to design-

nate the spacing of the odd acids. A summary of the data for the homologous series of saturated long-chain fatty acids is given in Table 31.

TABLE 31
Polymorphic Form and X-Ray Diffraction Data for Saturated Fatty Acids

Acid	Spacing	Angle of tilt	Acid	Spacing	Angle of tilt
Even	A	90°	Odd	A'	90°
Even	B	74°36'	Odd	B'	59°12'
Even	C	59°12'	Odd	C'	59°12'
			Odd	D'	52°29'

As previously mentioned, all aliphatic acids crystallize with double molecules oriented with their carboxyl groups in juxtaposition. Those series in which the chain is vertical (90° angle) do not show alternation in their physical properties while those with tilted chains do exhibit this phenomenon. The saturated fatty acid series appears in various crystalline modifications due mainly to variations in the angle of tilt. The spacings of a particular compound vary with the sine of the angle of tilt. However, polymorphic forms are observed without changes in angle of tilt, i.e., the transition $\alpha \rightarrow \beta$ for the odd acids with the C'- and B'-spacings does not involve any change in the β -angle of tilt.

In 1939, Francis and Piper (56) published a résumé covering the results of ten years of investigation on the crystal properties of the higher normal aliphatic acids and their methyl and ethyl esters. The long-spacing values for the fatty acids, tabulated in their report, are given, with their corresponding melting points, in Table 32. For completeness, melting points and long spacings, reported by others (45,57,58), are included. Owing to the fact that the acids are irreversibly converted below their melting points to the stable form, only one melting point is observed for each acid. The pure acids exhibit only monotropy and their polymorphic behavior is relatively uncomplicated compared with that of many of their derivatives. The various forms are readily distinguished by x-ray examination.

There is some confusion and even contradictory evidence relative to the proper conditions for preparing the various polymorphic forms of the pure acids, but the following general rules may serve as guides for preparation of each polymorph:

A- and A'-Spacing Forms. These forms were prepared by Piper *et al.* (53) by pressing stearic and palmitic acids upon a glass plate. They are not important forms and spacings for only a very few acids with these forms have been published.

TABLE 32
Melting Points and Long Spacings of the Saturated Fatty Acids (56)

Carbon atoms	Melting point, ° C.	Long spacing, Å.			
		A	B	C	
Even number					
10	—	—	—	23.00 (57)	
12	—	—	—	27.22 (57)	
14	54.4	—	34.9 (58)	31.60	
16	62.9	41.0 (58)	39.1	35.60	
18	69.6	46.6 (58)	43.75	39.75	
20	75.35	48.45	48.45	44.15	
22	79.95	—	52.95	48.3	
24	84.15	—	57.75	52.6	
26	87.7	—	62.2	56.25	
28	90.9	—	67.15	61.05	
30	93.6	—	71.4	65.2	
32	96.0	—	76.3	69.25	
34	98.2	—	80.5	73.3	
36	99.9	—	85.25	78.1	
38	101.6	—	90.0	82.1	
46	106.85	—	108.2	99.05	
Odd number					
		A'	B'	C'	D'
11	—	—	—	25.31 (57)	—
13	—	34.89 (57)	31.27 (57)	30.0 (58)	25.8 (58)
15	52.1 (58)	39.88 (57)	35.68 (57)	34.2 (58)	29.9 (58)
17	61.3	—	40.45	38.6 (58)	33.9 (58)
19	68.65	—	44.50	43.15 (58)	—
21	74.3	—	49.25	47.8 (58)	—
23	79.1	—	53.40	51.8 (58)	—
25	83.5	—	57.65	56.2 (58)	—
27	87.5–87.7 (45)	—	61.95 (45)	60.5 (58)	—
29	90.3	—	66.35	64.8 (58)	—
31	93.0–93.2 (45)	—	70.44 (45)	—	—
35	98.3–98.5 (45)	—	78.75 (45)	—	—

B-Spacing Form. This form is generally obtained by slow crystallization from nonpolar solvents.

B'-Spacing Form. Crystallization from solvents, irrespective of solvent, yields this form. It is also obtained from melt at normal rate of cooling.

C-Spacing Form. Rapid crystallization from polar solvents or solidification from melt produces the C-spacing modification.

C'-Spacing Form. C'-spacing forms are obtained from solidification of melts but they are rapidly transformed on cooling to the B'-form. The C'-spacing modification is retained only by very rapid cooling.

D'-Spacing Form. These modifications are rare. No details regarding their preparation have been found.

The α - and β -forms of the saturated fatty acids, which have the C or C' and B or B' long spacings, respectively, are the only two types commonly encountered. Acids having odd and even numbers of carbon atoms can be distinguished because: (1) solution of odd acids always deposits crystals having a B'-spacing regardless of the nature of the solvent, while with the even acids the form depends upon the polarity of the solvent and somewhat upon the rate of crystallization; and (2) from a melt the even acids crystallize in the modification with the C-spacing while the odd acids, although first deposited in the C'-spacing modification, on cooling are rapidly transformed to the B'-spacing modification, so that, under normal conditions, this latter B'-spacing is obtained when an odd acid is solidified from melt.

(c) Polymorphism of Salts of Fatty Acids

X-ray photographs of the sodium salts of the fatty acids were first obtained by Piper and Grindley (59,60). They found the long spacings of these salts were characteristic of long-chain compounds, exhibiting a uniform increase in spacing value with increasing number of CH_2 groups in the molecules. Piper (61) found that pure anhydrous potassium salts of the fatty acids, unlike the free acids, appear to have only one polymorphic form. For this reason, he claimed, they are very well suited for x-ray measurements for analytical purposes. When long-spacing values of the potassium salts with carbon atom content from 2 to 24 are plotted against the carbon content, two straight lines are obtained. One represents the acid salts, the other the normal (neutral) salts. From these data angles of tilt can be calculated. Such calculations show that the acid salts crystallize with vertical chains (90° angle of tilt) while the neutral salts are inclined at an angle of $45^\circ 41'$.

Ammonium salts were investigated by Kench and Malkin (62), who observed that a plot of the values for the long spacings of the salts with 7 to 18 carbon atoms gave two straight lines, one for the acid salts and the other for neutral salts. Crystallization from alcohol gave products exhibiting both sets of lines, those for the shorter of the two long spacings, (neutral salts) very intense, and those from the acid salts, considerably weaker.

Salts crystallized from diethyl ether gave only the longer spacings characteristic of the acid salts. The x-ray diffraction data for the potassium and ammonium salts mentioned above, together with some values for the lead salts from Trillat (63), are summarized in Table 33.

TABLE 33
Long Crystal Spacings of Salts of the Fatty Acids

Carbon atoms	Long spacing, A.		Carbon atoms	Long spacing, A.	
	Normal	Acid		Normal	Acid
<i>Potassium salts (61)</i>			<i>Ammonium salts (62)</i>		
1	6.4	—	7	—	22.8
2	9.13	—	8	19.6	25.1
3	11.4	—	10	24.2	30.2
4	—	14.90	11	25.4	32.2
5	15.55	17.07	12	27.1	35.0
7	19.16	—	13	29.6	37.7
8	22.3	—	14	31.5	40.9
11	27.45	—	15	33.0	43.2
12	30.2	35.53	16	36.1	45.8
13	31.85	—	17	36.4	47.9
14	33.95	40.45	18	38.4	50.8
15	35.8	42.9	<i>Lead salts (63)</i>		
16	37.9	45.29	6	20	
17	39.77	48.10	8	25.4	
18	42	50.47	10	30.6	
19	43.8	53.03	12	35.8	
20	46.45	55.63	14	41.2	
21	47.85	58.35	16	46.3	
22	50.72	60.78	18 ^a	51.3	
23	51.8	63.25	18 ^b	29.8 and 37.5	
24	54.45	65.94	18 ^c	50	

^a Stearate.

^b Oleate.

^c Elaidate.

(d) *Polymorphism of the Methyl and Ethyl Esters of Saturated Long-Chain Fatty Acids*

One of the earliest investigations of the x-ray diffraction of esters was published by Shearer (23) in 1925. Data were reported for ethyl esters by Francis *et al.* (58,64). X-ray diffraction data for methyl and ethyl esters were reported by Malkin (39) in 1931 and by Piper *et al.* (45) in 1934. A summary of the data pertaining to these esters is included in the previously mentioned review of Francis and Piper (56).

According to Malkin (39), methyl esters crystallize in layers of double molecules. A second modification is found only in the case of methyl esters of acids containing an odd number of carbon atoms. Ethyl esters crystallize in layers of single molecules and exist in two crystalline forms, a stable β -modification and an α -form, stable over only a limited range of temperature near the melting point. The α -modification exhibits only one short spacing at 4.2 Å., while the β -modification manifests the two short spacings usually attributed to long-chain fatty acids. Some crystal properties of fatty acid esters derived by means of x-ray diffraction are presented in Table 34.

TABLE 34

Polymorphic Forms and Data Obtained from X-Ray Diffraction for Methyl and Ethyl Esters

Form of ester	Length	Spacing	Angle of tilt
<i>Methyl</i>			
Metastable odd acids only	Single molecule	A	75°
Stable odd acids	Double molecule	B	67°31'
Stable even acids	Double molecule	B	63°
<i>Ethyl</i>			
Metastable	Single molecule	A	90°
Stable	Single molecule	B	67°30'

Evidence of the occurrence of polymorphism in the methyl and ethyl esters is considerably more complex than for the acids. The esters possess multiple melting points and exhibit both monotropic and enantiotropic polymorphism dependent upon their chain length and whether they contain an odd or an even number of carbon atoms in the chain. Polymorphism of the esters has been investigated with the aid of thermal data, i.e., melting points, cooling curves, etc., to a greater extent than by means of x-ray diffraction. Mumford and Phillips (65,65a) investigated the polymorphic behavior of a large number of pure ethyl esters and their binary mixtures. A summary of these data is given in Figure 8. Inspection of the curves indicates that throughout the homologous series the α -freezing points lie on a smooth curve but the β -melting points alternate.

The β -melting point curve of the esters having an even number of carbon atoms is higher than and distinct from that for the esters with an odd number of carbon atoms. On examination of the α -freezing-point and β -melting-point curves, it is seen that just as the α -melting-point curve intersects the β -melting-point curve of the odd esters at, or about, the C₁₇

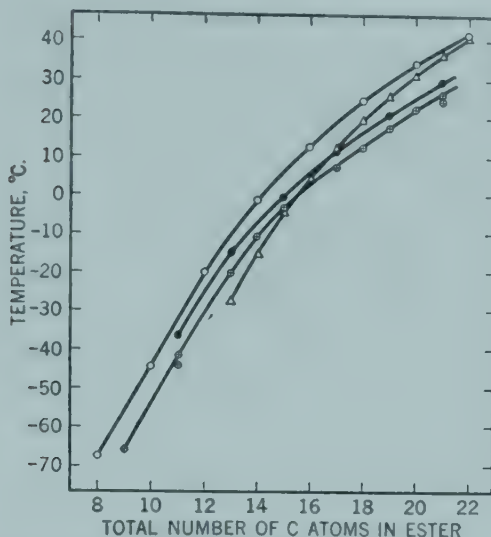


Fig. 8. Freezing and melting point curves of the ethyl esters of the saturated fatty acids (65a): ○, m.p. curve of the β -form of the even esters; ●, m.p. curve of the β -form of odd esters; Δ , f.p. curve of the α -form of the odd and even esters; $\oplus$ f.p. curve of the γ -form of the odd and even esters.

member of the series, so in the other direction it will intersect the β -melting-point curve of the even esters above C_{22} , i.e., the higher even members, like the odd members of the series, will exhibit enantiotropy.

Mumford and Phillips found that, in addition to the transparent α -form, ethyl esters can crystallize in two other modifications, namely, a higher-melting stable form, called the β -modification, and a lower-melting unstable form, called the γ -modification. They concluded from these investigations that ethyl esters of the fatty acid series from C_{12} upward exhibit three distinct kinds of alternation of polymorphic type as follows:

1. *Alternating monotropy*, with esters up to C_{16} ; the α -forms of both odd and even numbers being metastable and unobtainable except in mixtures.

2. *Alternating monotropy and enantiotropy* with esters from C_{16} to C_{22} ; the α -forms of the odd members being stable near the melting point, and those of the even members metastable but unobtainable.

3. *Alternating enantiotropy* with esters above C_{22} ; the α -forms of both odd and even members being stable in the vicinity of the melting point.

Evidence based on the observation relative to the existence of a $\gamma(C_1)$ -modification of the ethyl esters of the odd-numbered acids from C_9 to C_{21} indicates that these esters may be trimorphic. There has been no x-ray evidence for the existence of a γ -modification.

Smith (66) summarized the information available up to 1939 relative to the polymorphism of the ethyl esters as follows:

At least three kinds of polymorphism are observed. For the esters up to ethyl myristate, the opaque β -forms of both even and odd members are stable, and the transparent α -forms are metastable (*monotropic polymorphism*); from ethyl myristate to ethyl eicosanoate, the α -forms of the odd members are stable near the melting point and change enantiotropically to the β -forms on cooling; α -forms of the even members are metastable (except in mixtures) and change monotropically to the β -forms; above ethyl eicosanoate, the α -forms of both odd- and even-members are stable near the melting point (*monotropic polymorphism*). Data for the x-ray long spacings of the methyl and ethyl esters of the saturated long-chain fatty acids are summarized in Table 35.

TABLE 35

X-RAY LONG SPACINGS OF METHYL AND ETHYL ESTERS OF LONG-CHAIN FATTY ACIDS

Carbon atoms in acid	Long spacing, A.			
	A		B	
	Methyl esters		Ethyl esters	
14	—	38.8 ^a	—	—
15	23.6 ^a	41.8 ^a	—	—
16	—	43.45 ^{a,b}	—	22.9 ^{a,b}
17	26.0 ^a	46.3 ^{a,b}	27.1 ^a	24.75 ^{a,b}
18	—	47.95 ^{a,b}	—	25.80 ^{a,b}
19	28.4 ^a	50.8 ^{a,b}	29.8 ^a	26.95 ^{a,b}
20	—	52.30 ^{a,b}	—	27.6 ^{a,b}
21	30.9	55.25 ^{a,b}	32.4 ^a	29.35 ^{a,b}
22	—	57.02 ^{a,b}	—	29.90 ^{a,b}
23	—	60.0 ^{a,b}	—	31.50 ^{a,b}
24	—	61.70 ^b	—	32.15 ^{a,b}
25	—	64.55 ^b	—	33.60 ^{a,b}
26	—	66.15 ^b	—	34.45 ^{a,b,c}
27	—	—	—	35.8 ^{a,b}
28	—	70.80 ^b	—	36.65 ^{a,b}
29	—	73.75 ^b	—	38.1 ^{a,b}
30	—	75.21 ^b	—	38.75 ^{a,b}
32	—	79.95 ^b	—	41.1 ^{a,b}
34	—	84.15 ^b	—	43.45 ^{a,b}
36	—	89.3 ^b	—	46.3 ^a
38	—	93.0 ^b	53.55 ^a	48.05 ^a
46	—	121.7 ^b	—	57.45 ^a

^a T. Malkin, *J. Chem. Soc.*, 1931, 2796-2805.

^b F. Francis and S. H. Piper, *J. Am. Chem. Soc.*, 61, 577-581 (1939); F. Francis, S. H. Piper, and T. Malkin, *Proc. Roy. Soc., London*, 128A, 214-252 (1930).

^c S. H. Piper, A. C. Chibnall, and E. F. Williams, *Biochem. J.*, 28, 2175-2188 (1934).

Because of some confusion in the terminology of the various modifications, it needs to be noted that in Table 35 A-spacing is used to designate the polymorphic form with the vertical zigzag chain in the case of the ethyl esters, or the greatest β -angle (75°) in the case of the methyl esters. The B-spacing is assigned to the most stable forms with shorter long-spacings, corresponding to tilted chains. Thus, the A-spacing would correspond to the α -modification and the B-spacing to the β -modification, departing from the system used for the acids, where the C-spacing corresponds to the α -modification.

(e) *Polymorphism of Long-Chain Alcohols*

According to Malkin (43) normal long-chain primary alcohols crystallize in two modifications with spacing A, a vertical chain, and spacing B, a chain tilted at an angle of $55^\circ 40'$. The vertical-chain modification is the more stable form for the odd carbon series of alcohols, and the tilted-chain modification is more stable for the alcohols with an even number of carbon atoms. If the long spacing is plotted against the number of carbon atoms in the chain, two straight lines are obtained; the odd-numbered carbon alcohols lying on one, the even-numbered carbon alcohols on the other. However, below C_{16} the spacing for the even alcohols lies on the line for the odd-numbered alcohols. The C_{16} -alcohol gives two spacings, one on each curve. The C_{18} -alcohol crystallized from solvent gives a spacing which fits the curve for even-numbered carbon alcohols, but if fused, it gives a spacing on the line for the alcohols having an odd number of carbon atoms (43). X-ray diffraction data show that all normal aliphatic alcohols crystallize in double molecules with the hydroxyl groups in juxtaposition (Table 36).

TABLE 36
X-Ray Diffraction Data for *n*-Aliphatic Alcohols (43)

Alcohol	Length	Spacing	Angle of tilt
Odd and even carbon number below			
C_{16} or C_{18} ^a	Double molecule	A	90°
Even carbon number above C_{16} or C_{18} ^a	Double molecule	B	$55^\circ 40'$ ($51^\circ 55'$) ^b

^a C_{16} - and C_{18} -alcohols crystallize in both polymorphic forms.

^b Value from Wilson and Ott (67).

The x-ray diffraction of alcohols has also been investigated by Piper *et al.* (31,45) and by Francis *et al.* (64). Data for the values of the x-ray long spacings are collected in Table 37.

TABLE 37
 X-Ray Long Spacings of Aliphatic Alcohols

Carbon atoms	Long spacing, Å.	
	A	B
12	34.8 ^a	—
13	36.88 ^b	—
14	39.7 ^{a,b}	—
15	42.14 ^b	—
16	44.9 ^{a,b}	37.4 ^{a,b}
17	47.08 ^b	—
18	50.2 ^{a,b}	41.35 ^{a,b,c}
19	52.75 ^a	—
21	57.4 ^a	—
22	—	49.95 ^{a,c}
24	—	54.0 ^{a,c}
25	68.5 ^a	—
26	—	58.0 ^{c,d}
27	72.95 ^d	—
28	—	62.3 ^{c,d}
29	78.0 ^d	—
30	—	66.4 ^{c,d}
32	—	71.0 ^{c,d}
34	—	74.64 ^d
36	—	80.28 ^d

^a T. Malkin, *J. Chem. Soc.*, 1935, 726.

^b D. A. Wilson and E. Ott, *J. Chem. Phys.*, 2, 231–238 (1934).

^c F. Francis, F. J. E. Collins, and S. H. Piper, *Proc. Roy. Soc., London*, 158A, 691–718 (1937).

^d S. H. Piper, A. C. Chibnall, and E. F. Williams, *Biochem. J.*, 28, 2175–2188 (1934).

Wilson and Ott (67) measured the long spacings of several members of the homologous series of aliphatic *n*-alcohols. The values they obtained for the long spacings varied slightly from those reported by Malkin (43), and the calculated value for the angle of tilt of the β -modification was $51^\circ 55'$. They agreed, however, with most of the conclusions of Malkin, e.g., that all alcohols crystallize with double-molecular layers, and although the even-numbered carbon alcohols exhibit polymorphism and crystallize in both α - and β -modifications, only the former were found for the odd-numbered carbon alcohols. Although Wilson and Ott failed to observe two modifications of the odd-numbered alcohols, Meyer and Reid (68) concluded on the basis of cooling-curve data that the even and odd members of the series exist in both modifications.

In 1951 Kolp and Lutton (69) reported that *n*-hexadecanol and *n*-octadecanol can exist in three modifications, namely, α , sub- α , and β . The α -modification is the first form obtained from a melt; the sub- α -form is obtained by rapid chilling of the melt to room temperature; and the β -form is obtained by aging. The α - and sub- α - modifications crystallize with perpendicular chains. The α -form shows a single short spacing and the sub- α -form, three short spacings. The β -modification is the stable form, crystallizing with a tilted chain, and is obtained either from the α -forms or directly by crystallization from volatile solvents. Kolp and Lutton reported the data reproduced in Table 38 for these two alcohols.

TABLE 38
X-ray Diffraction of *n*-Hexadecanol and *n*-Octadecanol (69)

Alcohol	Long spacing, A.			Short spacing, A.		
	α	Sub- α	β	α	Sub- α	β
<i>n</i> -Hexadecanol	44.3	44.9	37.2	4.17 VS	4.09 VS ^a	4.30 M ^a
		(44.84) ^b	(36.84) ^b		3.73 M	4.08 VS
					3.64 S	3.60 S
<i>n</i> -Octadecanol	49.0	49.7	41.8	4.19 VS	4.09 VS	4.30 M
		(49.57) ^b			3.73 M	4.08 VS
					3.64 S	3.62 S

^a Unless otherwise defined, the symbols used here and throughout this chapter have the following equivalency: M = medium intensity; S = strong intensity; VS = very strong intensity; W = weak intensity of the x-ray diffraction line.

^b Figures in parentheses are from Wilson and Ott (67).

(f) Polymorphism of Unsaturated Acids

One of the earliest known examples of the occurrence of polymorphism in long-chain fatty acids was that observed in the course of making certain thermal measurements with oleic acid. X-ray diffraction examination of the various crystalline modifications of this acid were not made until 1946 when Lutton (70) reported the following data: (1) m.p. 13.3° C., long spacing 40.5 Å., main short spacings 4.64 Å. (M), 4.19 Å. (S), 3.80 Å. (M) and (2) m.p. 16.2° C., long spacing 84.4 Å., main short spacings 4.65 Å. (VS), 4.37 Å. (M), 4.83 Å. (M) and 3.67 Å. (VS). See footnote Table 38 for significance of letters following numerical value of spacing.

The low melting-point form has a regular, tilted, double-molecule structure. The higher-melting form appears to be four molecules in length although it may be only two (with a long spacing of 42.2 Å.). In any case, it

does not follow the usual pattern of aliphatic monocarboxylic acids. Intensity patterns of successive reflections show that the orders 2 to 9 are completely absent and there is no evidence for the usual alternation of strong intensities of the odd orders of reflection.

Unsaturated acids were the subject of one of the early investigations of Müller and Shearer (24). They reported long spacings for oleic, 36.2; elaidic, 48.3; iso-oleic, 35.9; erucic, 46.3; and brassidic, 59.8 Å. These data demonstrate that different isomers of the same chain length have different long spacings indicative of different types (tilts) of chain.

Lutton and Kolp (71) investigated the x-ray diffraction of *trans*-octadecenoic acids with the double bond at the 6th through the 12th position. They showed that such compounds do not exhibit polymorphic modifications. Those unsaturated acids with a double bond at an odd-numbered carbon atom, e.g., elaidic and vaccenic acids, have greater long spacings and lower melting points than those having a double bond at an even-numbered carbon atom. The former crystallize with their chains perpendicular, and the latter with the chain tilted with respect to the carboxyl plane: (1) acids with a double bond at the 7th, 9th, and 11th carbon atom have a long spacing of 49.5 Å., main short spacings 4.13VS and 3.74S; (2) acids having a double bond at the 6th, 8th, 10th, and 12th carbon atom, long spacings 45.5 Å., main short spacings 4.61S, 4.43S, and 3.17S. From intensity patterns individual pure acids can be identified, e.g., in this manner 9-elaidic and 11-vaccenic acids can be differentiated.

Benedict and Daubert (72) investigated the x-ray diffraction of vaccenic acid which had been demonstrated by infrared absorption methods to have a *trans* double bond (73). In Table 39 there are given the melting points and x-ray spacings for both synthetic and natural vaccenic acids and, for comparison, elaidic acid. The spacings for synthetic vaccenic acid agree very well with those for elaidic acid. The shorter long spacing for the natural vaccenic acid was attributed to crystallization of this sample in a form with a different degree of tilt, i.e., a different poly-

TABLE 39
X-ray Diffraction of Elaidic and Vaccenic Acids (72)

Acid	Melting point, ° C.	Long spacing, Å.	Short spacing, Å.
Elaidic	44.5	48.9	4.12 VS, 3.74 S, 3.65 S
Vaccenic (synthetic)	44.0	48.9	4.12 VS, 3.71 S, 3.66 S
Vaccenic (natural)	39.9	42.5	4.16 VS, 3.84 S, 3.68 M

morphic form. Vaccenic acid prepared by hydrogenation of β -eleostearic acid revealed x-ray patterns identical with those of the natural vaccenic acid.

(g) Polymorphism of Aliphatic Ketones

X-ray diffraction studies of ketones are of historical interest because as early as 1925 analyses of the data obtained with these compounds led to the establishment of two important conclusions regarding the x-ray spacings of long-chain compounds. Saville and Shearer (25) showed that methyl ketones crystallize with two molecules between successive reflecting planes, but that for all other ketones the repeating unit is a single molecule. Consideration of this fact, along with the diffraction patterns of other groups of compounds, i.e., acids with an active COOH group and hydrocarbons with no active group, led to the conclusion that all molecules with active groups crystallize as double molecules while those with no active groups appear as single molecules between reflecting layers. As the double-molecule unit seemed to be associated with active groups, it was logical to assume that the molecules were arranged with these active groups in juxtaposition, which assumption has since been confirmed by measurements on many compounds. A study of the diffraction of ketones led Shearer (40) to calculate from intensity patterns of the successive orders the mathematical relations between such patterns and the position of the carbonyl group on the chain and to show how these relationships could be used for purposes of chemical identification.

Long x-ray spacings and melting points for a number of aliphatic ketones are given in Table 40.

(h) Polymorphism of Dicarboxylic Acids and Other Derivatives

The melting points of dicarboxylic acids exhibit a striking example of the alternation between odd- and even-numbered carbon atoms. Caspari (37) showed experimentally that dicarboxylic acids with an odd number of carbon atoms contain four molecules per unit cell and a long spacing equal to twice the length of the dicarboxylic acid, while the dicarboxylic acids with an even number of carbon atoms contain only two molecules to the unit cell, which is only one molecule in length. In his discussion of zigzag structures and alternations in the properties of odd- and even-numbered compounds, Müller (36) showed theoretically why this phenomenon should be expected. For the even-chain dicarboxylic acids, the end-group carboxyls are so arranged that a single molecule constitutes a

TABLE 40
Melting Points and X-Ray Long Spacings of Aliphatic Ketones (25)

Ketone	Melting point, ° C.	Long spacing, Å.
Methyl- <i>n</i> -tridecyl	39.5	42.4
Methyl- <i>n</i> -pentadecyl	48-48.5	47.6
Methyl- <i>n</i> -hexadecyl	52	50.0
Methyl- <i>n</i> -heptadecyl	55.5-56	52.9
Ethyl- <i>n</i> -pentadecyl	52.5	25.2
Ethyl- <i>n</i> -heptadecyl	59.5-60	27.3
Propyl- <i>n</i> -pentadecyl	50	26.3
Propyl- <i>n</i> -heptadecyl	56	28.9
Di- <i>n</i> -hexyl	30	18.7
Hexyl- <i>n</i> -undecyl	45	25.2
Hexyl- <i>n</i> -pentadecyl	54	31.1
Hexyl- <i>n</i> -heptadecyl	62	33.6 (30.8) ^a
Octyl- <i>n</i> -Eicosyl	74.4	38.9 (31)
Nonyl- <i>n</i> -Nonadecyl	75.0	38.9 (31)
Di- <i>n</i> -undecyl	69.5	31.6
Undecyl- <i>n</i> -heptadecyl	74.7	38.9 (31)
Di- <i>n</i> -tridecyl	69.5	37.0
Tridecyl- <i>n</i> -pentadecyl	74.7	38.9 (31)
Di- <i>n</i> -tetradecyl	80.8	38.65 (31)
Di- <i>n</i> -pentadecyl	76-76.5	41.1
Di- <i>n</i> -heptadecyl	82.5	47.2

^a Saville and Shearer reported two long spacings for hexyl-*n*-heptadecyl ketone which they attributed to two polymorphic forms. This was one of the first examples of the detection of polymorphism from x-ray diffraction measurements.

repeating unit. For the odd members two molecules are required before a completely repeating unit is obtained. Trillat (74) published x-ray data on several dicarboxylic acids and Normand *et al.* (75) investigated both the dicarboxylic acids and their methyl and ethyl esters. A summary of their results is presented in Table 41.

Dimorphism of the dicarboxylic acids has been established by Caspari (76) who showed, in 1929, that besides the α -modification (shown in Table 41) azelaic acid (C₉) could exist in a β -form obtained by rapid crystallization of a saturated aqueous solution. DuPré la Tour (77) similarly demonstrated two forms of pimelic acid (C₇).

Lutton *et al.* (78) reasoned that the relative intensities of the long spacings of the dihydroxy derivatives of octadecenoic acid (dihydroxy-octadecanoic acid) would give a clear-cut distinction between individual members of the series because of differences in relative positions of the

TABLE 41

Melting Points and X-Ray Long Spacings of Dicarboxylic Acids and Their Methyl and Ethyl Esters

Carbon atoms	Dicarboxylic acids		Diethyl esters	
	Melting point, ° C.	Long spacing, Å.	Melting point, ° C.	Long spacing, Å.
4	180	4.5 (74)	—	—
6	148	7.0 (74)	—	—
7	149	7.6 (74)	—	—
8	140	9.3 (74)	—	—
9	107 (106)	9.56 (9.6) (74)	—	—
10	127	11.4	—	—
12	129	13.25	—	—
13	113.5	13.3	20	22.7
14	126.5	15.4	27	23.7
14	—	—	55	42.1 ^a
16	125	17.4	—	—
18	124	19.55	43	28.5
18	—	—	71	50.5 ^a
22	123.8	23.6	56	33.6
26	123.5	27.8	—	—
30	—	—	74	43.7
34	123	35.9	80	49.0

^a Dimethyl ester.

strongly diffracting hydroxyl groups. The dihydroxy acids prepared from unsaturated acids were divided into four groups, namely, hydroxy acids derived from low-melting unsaturated acids having their double bonds respectively at an odd-numbered or even-numbered carbon atom, and the corresponding high-melting hydroxy acids derived from the same types of acids. From data obtained with the dihydroxystearic acids, odd- and even-hydroxy-substituted acids can be differentiated by their short spacings. The position of the OH-groups can be established by comparisons of intensity patterns of successive reflections of the long spacings.

A series of such patterns are reproduced in Figure 8a from the publication of Lutton *et al.* (78). They illustrate the manner in which a set of standard patterns can be used in the identification of an unknown dihydroxy acid by a fingerprint-type of matching without any mathematical calculations. Diffraction data for the four groups of dihydroxy derivatives of stearic acid are given in Table 42.

Conversion of octadecenoic acids to dihydroxy acids and the dihydroxy acids to aldehydes and the aldehydes to dinitrophenylhydrazones followed

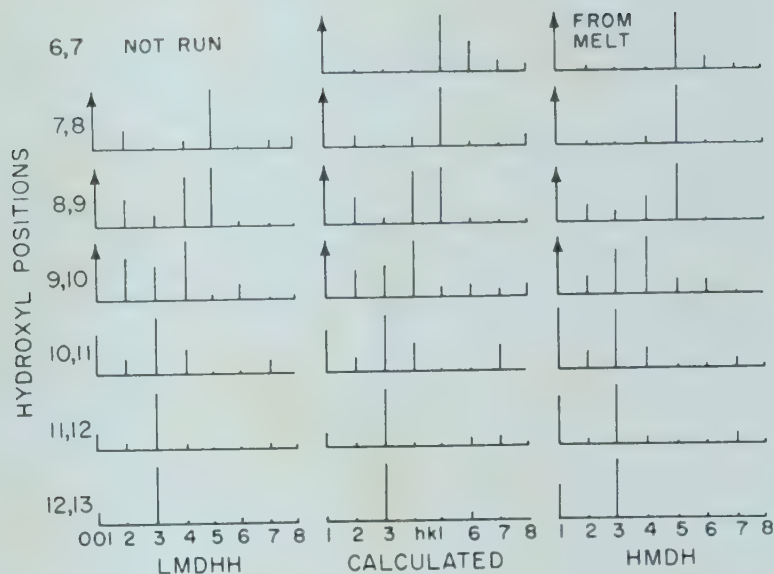


Fig. 8a. Position of the hydroxyl group (78).

by x-ray examination affords a somewhat roundabout means for the identification of the original acids. Stewart, Huber, and Lutton (79) compared the diffraction of a series of such derived compounds with the diffraction of dinitrophenylhydrazones prepared from authentic alde-

TABLE 42
X-ray Long Spacings of Dihydroxystearic Acids (78)

Position of hydroxyls	Long spacing, A. ^a	Long spacing, A. ^b	Molecules per unit cell
6,7	22.2 (44.4) ^c	22.5 (45.0)	Single
7,8; 9,10; or 11,12	38.8 ^c	42.2	Double
8,9; 10,11; or 12,13	45.5 ^c	43.9	Double
6,7	45.5 ^d	45.4	Double
9,10	48.9 ^d	48.7	Double

^a Low-melting dihydroxystearic acids.

^b High-melting dihydroxystearic acids.

^c Crystallized from solvent.

^d Crystallized from melt.

hydes. Malkin and Tranter (80) reported the melting points and x-ray diffraction data for the dinitrophenylhydrazones of *n*-aliphatic aldehydes. They found an increment of 1.4 Å. per CH₂ group in the long spacings for the homologous series, indicating a structure with a double-molecule layer

tilted at an angle of about 34° to the reflecting plane. A summary of the dinitrophenylhydrazone data of these two groups is given in Table 43.

TABLE 43

Long Spacings and Melting Points of 2,4-Dinitrophenylhydrazones of Aliphatic Aldehydes

Total carbon atoms	Melting point, $^\circ\text{C}.$ ^a	Long spacing, A. ^a	Long spacing, A. ^b		Authentic sample
1	166	7.33, 10.38	—	—	—
2	167.5	9.40	—	—	—
3	155	10.95, 9.64	—	—	—
4	119	13.5	—	—	—
5	106	15.08	—	—	—
6	105	16.34	16.2 ^c	—	16.3
7	106	17.78	—	—	17.7
8	105.5	19.15	19.4 ^c	19.2 ^d	19.3
9	106.5	19.6	19.9 ^c	19.7 ^d	19.8
10	106	21.12	21.0 ^c	21.1 ^d	21.2
11	106.5	22.38	22.3 ^c	22.3 ^d	22.6
12	106	23.95	—	—	—
13	106.1	25.4	—	—	—

^a T. Malkin and T. C. Tranter, *J. Chem. Soc.*, 1951, 1178–1179.

^b C. B. Stewart, W. F. Huber, and E. S. Lutton, *J. Am. Chem. Soc.*, **73**, 5903–5904 (1951).

^c Specimen derived from *cis*-octadecenoic acid.

^d Specimen derived from *trans*-octadecenoic acid.

6. Polymorphism of Glycerides

(a) Introduction

The "double" or "triple" melting-point phenomena observed with triglycerides has been known for many years. As early as 1849, Heintz (81) showed that if molten tristearin is quickly solidified, it remelts at $52^\circ\text{C}.$, but as the heating continues it resolidifies and melts again about $65^\circ\text{C}.$ Much later, Guth (82) observed a "double" melting of tristearin, and Duffey (83) described the "triple" melting of this compound at 52, 64.2 and $69.7^\circ\text{C}.$ These different melting points were attributed to isomeric forms but the variation in the numerical values reported resulted in considerable confusion because they were measured by various procedures and with preparations obtained by various and often undescribed means. Ferguson and Lutton (52), in an early review of the polymorphism of triglycerides,

listed seven melting points for β -laurodistearin, 36, 52, 56.5, 59.8, 60.5 and 68.5° C.

The observation of multiple melting points stimulated an interest in the study of polymorphism of glycerides but it was not until Malkin and co-workers in England investigated the polymorphism of glycerides by means of x-ray diffraction that a clear understanding of this phenomenon was obtained. In the decade before World War II, Malkin and co-workers published a series of papers which clearly established that multiple melting points resulted from polymorphism. Work of this group was discontinued during the war but was resumed about the middle of the 1940's, concomitantly with the investigations on the same subject by Lutton and co-workers and Daubert and his colleagues in the United States. Including the prewar contributions of Malkin and co-workers, these three groups contributed over fifty publications on x-ray diffraction and polymorphism of glycerides, more than forty of which appeared between 1945 and 1955. The combined results of these investigations clarified much of the confusion arising from prior thermal studies. They established as a fundamental principle that it is not possible to discuss the crystal, thermal, or x-ray properties of a glyceride without first defining its specific polymorphic form. Thus, a specific melting point can be ascertained only after suitable criteria have been applied to establish that a single pure polymorph is being dealt with. The various melting points reported for β -laurodistearin undoubtedly originated from measurements of different forms and mixtures of polymorphic forms. Similarly, x-ray diffraction patterns, cooling or heating curves, and other thermal data need to be obtained on single polymorphic modifications, otherwise it is not possible to obtain concordant data from repetitive measurements.

While the x-ray diffraction patterns have contributed considerably to an understanding of the nature of the polymorphism of glycerides, this has not occurred without some confusion. The polymorphism of the glycerides is relatively complicated and even the simplest triglycerides exhibit three or four polymorphic modifications, and mixed glycerides, particularly those containing acid chains of markedly different lengths, may crystallize in a number of additional modifications. The difficulties in understanding complexities involved in the polymorphism of glycerides have not been lessened by differences in viewpoints which have arisen between the various investigators in this field. Carter and Malkin (84) considered that the simpler glycerides can assume four polymorphic forms as follows:

1. A γ -modification, which is the lowest melting form and is called,

from its appearance, glassy or vitreous. This form shows no alternation of properties for odd and even carbon chain lengths and, very probably, crystallizes with the long chains perpendicular to the plane of the reflecting surfaces. Significantly, x-ray diffraction patterns have failed to reveal for this form any long spacing and only one diffuse short spacing at about 4.2 Å. The form is apparently unique in triglycerides. In structure it is considered by some workers to be that of a glass or liquid crystal. It is obtained only from a melt by rapid cooling.

2. An α -form having an intermediate melting point. It is nonalternating for odd and even carbon chains; and its long chains are perpendicular to the reflecting planes. The x-ray diffraction of this form reveals the greatest long-spacing values of the various modifications, which are consistent with the perpendicular chains. It gives a single sharp short spacing about 4.2 Å. The α -form is obtained from a melt on slow cooling or from the γ -form near the γ -melting point. It is a general form for all glycerides.

3. A β' -type structure, intermediate in melting point between the α - and β -polymorphs. This form is usually associated with a tilted chain, although perpendicular β' -forms have been observed. The long spacing may be equal to the α -form, the β -form, or it may be intermediate between the two. It usually exhibits two, but occasionally more, strong spacings at about 4.2 and 3.8 Å., by which it can usually be distinguished from its polymorphs.

4. A β -form, which is the most stable modification and has the highest melting point. It exhibits alternation of properties between odd and even carbon chain lengths and has a tilted long chain. It can be obtained by very slow cooling from a melt and is characteristic for nearly all triglycerides. Its x-ray long spacing is one of the shortest of the polymorphic forms of a specific glyceride and it exhibits a characteristically strong short spacing at 4.6 Å.

Three groups of workers have disagreed with Malkin's (85-87) classification of the polymorphic forms of triglycerides, and each group independently arrived at the conclusion that Malkin and co-workers erred in their association of melting points and x-ray spacings. Lutton (85) failed to observe the vitreous or glassy form reported by Malkin for tristearin and, from the results of investigations with scores of glycerides, concluded that there does not exist a glassy form, with a diffuse 4.2 Å. short spacing, but without any long spacing. Malkin's vitreous form was explained as a variation in melting point during stabilization. "For a given form of a given glyceride actual variation of complete melting point with extent of stabilization is common and must be the basis for the excess

characteristic melting points which have been previously reported" (88).

Lutton also maintained that the real problem is not whether a form, which is actually crystalline, is called a glass, but rather what properties, including x-ray diffraction lines, are truly associated with the lowest melting point. Lutton proposed that the lowest melting point modification be called the α -form in conformance with customary practice. The β' - and β -forms would then account for the other two known melting points and eliminate the necessity for four modifications required by Clarkson and Malkin (89) for tristearin, as opposed to the observations of many investigators who have detected only three melting points for this compound.

In a review of the polymorphism of saturated even chain-length glycerides, Lutton (90), using tristearin as a type compound for triglyceride polymorphism, presented the three typical x-ray patterns characteristic of the three modifications of this compound (Fig. 9). The short spacings



Fig. 9. Schematic representation of x-ray patterns for the three forms of tristearin (90).

characteristic of the aforementioned three modifications are given in Table 44. The cross-sectional arrangement of the chains, which accounts for these main short spacings, can be indicated as in Figure 10, where the black circles represent the chain axes and the short spacings are indicated.

Characteristic x-ray and melting-point data for the several forms of tristearin described by the above-mentioned two schools are collected in

TABLE 44

Characteristic Short Spacings of Different Forms of Even Chain Saturated Triglycerides (90)

Form	Characteristic short spacing
α	A single, strong, short spacing at 4.15 Å.
β'	Usually two (but occasionally more) strong, short spacings at 4.2 and 3.8 Å.
β	A strong (usually strongest), short spacing at 4.6 Å.

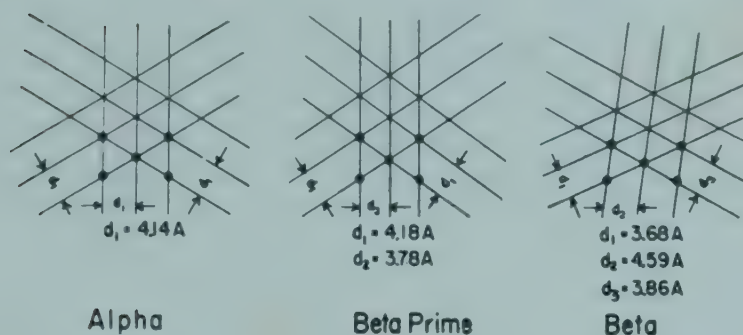


Fig. 10. Cross-sectional structures of triglyceride chains (90).

Table 45. Clarkson and Malkin added the β' -form of tristearin from later investigations (89). On a basis of melting points only, the following correlation of nomenclature can be applied: Lutton's $\alpha \approx$ Malkin's γ ; Lutton's $\beta' \approx$ Malkin's α ; and Lutton's $\beta \approx$ Malkin's β . Except for the β -modifications such a transformation would not give agreement based on the x-ray spacing data. It is not possible to resolve the differences between

TABLE 45
Comparison of Thermal and X-ray Diffraction Data for Tristearin

According to Lutton (85)				According to Malkin (84)			
M.p., ° C.	Main short spacing, Å.	Long spacing, Å.	Name for form	M.p., ° C.	Main short spacing, Å.	Long spacing, Å.	Name for form
54	4.14	50.6	α	54.5	4.2	—	Vitreous
64	3.78, 4.18	46.8	β'	65.0	4.2	50.6	α
73.1	3.68, 3.84, 4.61 5.24	45.15	β	71.5	3.7, 3.9, 4.6, 5.3	45	β

the two systems on nomenclature alone. The addition of the β' -modification by Malkin (89) results in the proposal by his group of four polymorphic modifications of tristearin, whereas Lutton and other investigators maintain that only three exist. The problem of establishing a common basis for transforming the data of one group to the system of the other is further complicated when applied to mono- and di- and mixed triglycerides which exhibit additional polymorphic forms. Lutton and Jackson (91) comment that β' in Malkin's system, when applied to monoglycerides, may be either sub- α or β' in their system; from the data available it is not possible to decide which is correct.

Evidence of the existence of additional polymorphic forms with melting points intermediate between the α - and β' - or between the β' - and β -modifications in mixed triglycerides of different chain lengths has necessitated the introduction of the terms sub- α , sub- β , β'' , etc., as will be discussed later. These additional terms make any attempt to transpose data expressed in one system to the corresponding terms of the other fraught with potential inaccuracies. In this review no such transpositions have been attempted. The interested reader must bear in mind both systems, and in considering any published literature, he must be sufficiently familiar with each system to recognize which is being employed and to make such transformations from one system to the other as may be possible. The system suggested by Lutton has been used by most workers in the United States and in particular by those groups who have published the greatest amount of x-ray diffraction data.

In a review published in 1952, Malkin (92) gave in considerable detail his reasons why the proposal of the three groups of American workers *that the concept of the glassy state of triglycerides should be eliminated and the lowest melting point called the α -form* should be discarded in the best interest of the subject of polymorphism and x-ray diffraction of glycerides. In a lengthy discussion Malkin summarized: (1) evidence favoring the existence of the vitreous form; (2) arguments intended to refute the suggestion of Lutton (85) that several of his (Malkin's) melting points arise from the effect of degree of stabilization; and (3) interpretations of cooling- and heating-curve data designed to demonstrate that this system is more closely correlated with experimental observations.

Malkin objected to Lutton's (90) discussion of triglycerides based on tristearin as a type compound. He contended that such structures as are shown in Figure 10 can be determined only on the basis of more complete crystal analysis from x-ray diffraction measurements on single crystals. No data of this type have as yet become available for any β' - or β -phases of the triglycerides. Until such measurements are forthcoming, any association of polymorphic forms with definite crystal structure, such as Lutton's system based on the characteristic short spacings, (Table 44) is premature.

Clarkson and Malkin (93) proposed a tuning-fork structure of glycerides where the observed spacing is double the length of the acid chain (Fig. 11) with alternating molecules regarded as lying head-to-tail across the reflecting planes either vertically or tilted. Lutton (94) and Jackson and Lutton (95) found that polymorphic forms of many mixed saturated triglycerides have long-spacing values which are abnormally

large, too large to permit their associated crystal structures to be classified as typical double chain-length structures. They proposed a triple chain structure and later even a quadruple structure to account for these abnormally great long spacings. Figure 11 illustrates the various types of geometric arrangements for various chain lengths based on the tuning-fork hypothesis. The common type of structure for saturated glycerides is a double structure with reversed tuning forks (handles beside prongs) forming an essential part of the repeated structural unit. If the chain lengths in a given glyceride structure differ by four or more carbon atoms, triple structures may appear, where the short chains have sorted

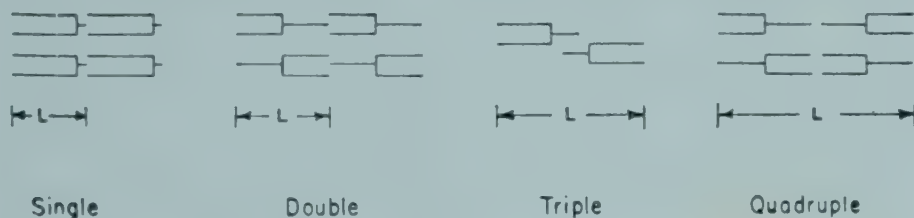


Fig. 11. Chain-length multiplicity of triglycerides (90).



Fig. 11a. Unsymmetrical or "chair" arrangement of triglycerides (90).



Fig. 11b. Disaturated-glyceride arrangement (90).

from long chains by a slipping of the reversed tuning forks until they are handle-beside-handle to effect a better "space filling." In the case of unsymmetrical glycerides (96) tuning-fork arrangements may give way to triple chain-length, "chair-type" arrangements (Figure 11a). Mixed oleic-saturated glycerides show considerable tendency toward triple structure formation. Such mixtures may involve a segregation of saturated from unsaturated chains giving the disaturated arrangement observed in Figure 11b. Substantial chain length differences may also give rise to quadruple chain-length structures which seem to be essentially doubled double structures. Single chain-length structures appear only when a very great difference in chain length exists (97).

The postulation of chain-length multiplicity has further complicated the problem of polymorphism and the designation of polymorphic forms of the glycerides. Lutton proposed the use of a number following the Greek letter designating the modification, to indicate the chain-length multiplicity (94). Thus, α -2 would indicate the α -modification with a double chain length; β' -4 would indicate the β' -modification with a quadruple chain length; β -3 would indicate the β -modification with a triple chain length; sub- α -1 would indicate the sub- α -modification with a single chain length; and so on. If no number follows the Greek letter designation, the more common double chain-length structure would be assumed.

(b) *Monoglycerides*

The 1-monoglycerides, 1-monostearin and 1-monopalmitin, were shown by Fisher *et al.* (99) in 1920 to have double melting points. Rewadikar and Watson (100) measured the melting points of 1-monolaurin, 1-monomyristin, 1-monopalmitin and 1-monostearin and demonstrated that they exist in two polymorphic modifications. The first x-ray diffraction confirmation of the polymorphism of these 1-monoglycerides is attributed to Malkin and El Shurbagy (101) who reported thermal and diffraction measurements of the 1-monoglycerides from 1-monodecoin to 1-monostearin. Their values are given in Table 46.

TABLE 46
Melting Points and Long Spacings for 1-Monoglycerides (101)

1-Mono- glyceride	α -Form		β' -Form		β -Form	
	M.p., ° C.	Long spacing, A.	M.p., ° C.	Long spacing, A.	M.p., ° C.	Long spacing, A.
Decoin	27	37.2	49	32.9	53	32.9
Undecoin	36.5	40.2	52	35.2	56.5	35.2
Laurin	44	43.2	59.5	37.3	63	37.3
Tridecoin	50	46.2	61	39.6	65	39.6
Myristin	56	—	67.5	41.5	70.5	41.5
Pentadecoin	62	51.3	69	43.8	72	43.8
Palmitin	66.5	—	74	45.8	77	45.8
Heptadecoin	70	—	74.5	48.2	77	48.2
Stearin	74	58.3	79	50.0	81.5	50.0
Arachin (103)	—	—	—	—	84	54.4

All of the 1-monoglycerides examined were shown to exist in three modifications: (1) an α -form with vertical rotating chains, no alternation

between odd- and even-numbered carbon atoms, and low melting points; (2) a β' -form with intermediate melting points, inclined chains, and alternating melting points; and (3) a β -form with long spacings identical to those of the β' -form, having the highest melting points and, like the β' -modification, inclined chains and alternating melting points.

The α -modification is the first to appear from a melt. It will transform to the more stable β' -form and finally, much more slowly to the stable β -modification. The β' -form is usually obtained by very rapid crystallization from solvents and the β -modification by very slow crystallization. Although the β' - and β -forms have identical long spacings, they can be differentiated readily by their short spacings, the former exhibiting two short spacings at 3.86 and 4.24 Å. and the latter at 3.94 and 4.65 Å. The α -modification shows a single short spacing at 4.2 Å. associated with a few very weak lines which Malkin believes may arise from traces of other forms.

Lutton and Jackson (91) re-examined the x-ray diffraction of 1-monostearin and 1-monopalmitin, and found the four polymorphic modifications shown in Table 47.

TABLE 47

Melting Points and X-ray Long Spacings of 1-Monostearin and 1-Monopalmitin (91)

1-Mono- glyceride	Sub- α -form		α -Form		β' -Form		β -Form	
	T.p., ° C. ^a	Long spacing, Å.	M.p., ° C.	Long spacing, Å.	M.p., ° C.	Long spacing, Å.	M.p., ° C.	Long spacing, Å.
Monostearin	49	50.3	74	50.2	78	50.1	81.5	50.1
Monopalmitin	39	45.5	66.9	45.6	74.6	45.25	77.0	45.6

^a Sub- α -transformation temperature.

The sub- α -form undergoes a reversible transformation to the α -form and therefore has no melting point. It exhibits a single short spacing, a strong line at 4.15 Å., and other weaker lines at 3.9, 3.75, and 3.55 Å. The α -polymorph is the form with the lowest complete melting point. It exhibits a strong 4.15 Å. short spacing and other weak lines. The β' -form has an intermediate melting point and two characteristic short spacings, a strong line at 4.15 Å. and a line of medium intensity at 3.65 Å. The β -form has the highest melting point and a single strong short spacing at 4.55 Å. It is the only thermodynamically stable form. Lutton and Jackson (91) pointed out the following differences from the work reported by Malkin and El Shurbagy (101): (a) four polymorphic forms have been

found (Malkin and El Shurbagy report only three); (b) the β -modification was found to be the only thermodynamically stable form; (c) the β' -form was obtained only from solvent; and (d) all four forms have very nearly the same long spacings and appear to be tilted, double chain-length structures. (Malkin and El Shurbagy assigned a vertical chain to the α -form.)

Lutton comments that "it is uncertain whether Malkin's so-called β' -data should be properly regarded as pertaining to the β' - or to the sub- α -form. From the reported spacings and description of procedure no decision can be made." Malkin (92) maintains that the transition from the α -form to the sub- α -form is not genuinely reversible but only appears so because of the slow rate of the α - to β' -transition. The sub- α -form is considered by him to be noncrystalline, in the ordinary sense of the term.

Filer *et al.* (102) considered the data of Malkin too incomplete for satisfactory identification of the glycerides isolated from natural products by comparison with x-ray data on synthetic monoglycerides. They published a complete list of the "d," or interplanar, short spacings for the stable β -modification of the 1-monoglycerides with even-numbered carbon chains from monodecain to monostearin and of monoelaidin. Long spacings for the stable, β -modification of these compounds were also included. They showed by means of an equation for the straight line relating the increase in long spacing to the number of carbon atoms in the glyceride, that the long spacings of successive members could be computed and that such computed values were in good agreement with the observed ones. The values for their spacings are in good agreement with those of Malkin (Table 46). The β -angle of tilt for these 1-monoglycerides in the stable β -form was calculated to be $58^{\circ}41'$.

Carter and Malkin (84) have criticized the short-spacing data of Filer *et al.* (102), claiming that many of the long list of short spacings they found, in contrast to the very few reported in most measurements of the glycerides, were due to successive orders of reflections of long spacings from the CuK_{β} -line unfiltered from the CuK_{α} and that most of the remaining arose from the nylon holders in which their samples were supported.

Sidhu and Daubert (103) added 1-monoarachidin (glyceryl-1-eicosanoate) to the list of monoglycerides which have been investigated by x-ray diffraction. The values they observed for the long spacings of the stable β -form only of this monoglyceride are included in Table 46 with the data obtained by Malkin and El Shurbagy (101).

The 2-monoglycerides have been shown to occur to the extent of 5 to

8% of the total monoglyceride content of commercial monoglycerides (103a). Early investigations of Daubert and Clarke (104) showed that these monoglycerides had only one melting point. They probably do not exhibit polymorphism. The melting points and x-ray short and long spacings of five 2-monoglycerides containing even chains with 10 to 18 carbon atoms were included in the studies of monoglycerides by Filer *et al.* (102). The single polymorphic forms reported were shown to have melting points about 10 degrees lower than those of the corresponding 1-monoglycerides and a smaller angle of tilt, $45^{\circ}19'$. Long spacings, melting points, and the strongest short spacings of these 2-monoglycerides are collected in Table 48. The strongest short spacings were reported as 4.65 A. (S), 4.4 A. (VS), and 3.9 A. (VS).

TABLE 48
Melting Points and X-ray Long Spacings of 2-Monoglycerides (102)

2-Monoglyceride	M.p., ° C.	Long spacing, A.
Caprin	40.4	29.4
Laurin	51.0	32.8
Myristin	61.2	36.2
Palmitin	68.5	40.1
Stearin	74.5	43.8

The values in Table 48 are in excellent agreement with those of Bevan and Malkin included by Malkin in his review (92) as heretofore unpublished data. These workers considered the long spacings to correspond to double moleculese tilted at an angle of $44^{\circ}30'$.

Carter and Malkin (84) measured the x-ray diffraction of four monoglycerides of unsaturated acids, 1-monoerucin, 1-monobrassidin, 1-monoolein and 1-monoclaidin. They interpreted the thermal data to indicate the existence of four forms, although only one long spacing, namely, that for the most stable β -modification, was observed. Short spacings showed the existence of a β' - as well as the β -form. Monoglycerides of *trans*-unsaturated acids give the same side spacings as saturated glycerides. Derivatives of *cis*-acids give appreciably different spacings. Carter and Malkin explained this difference by showing that, while a *trans*-bond caused no appreciable change in the alignment of the hydrocarbon chain, a *cis*-bond brings about a decided change. Melting points and x-ray spacings for these unsaturated monoglycerides are included in Table 49. The observed long spacings in all cases indicate double-chain molecules.

TABLE 49

Melting Points and X-ray Long Spacings of Monoglycerides, Monoacid- and Diacid-diglycerides of Unsaturated Acids

Glyceride	Vitreous	α	β'		β	
	M.p., ° C.	M.p., ° C.	M.p., ° C.	Long spacing, Å.	M.p., ° C.	Long spacing, Å.
1-Monoerucin (84)	15	36	47	—	50	58.3
1-Monobrassidin (84)	37	62	68.5	—	71	58.8
1-Monoolein (84)	12.5	25	32	—	35	49.5
1-Monoelaidin (84)	29.5	42	56	—	58.5	50.3
1,3-Dierucin (84)	—	41	44.5	47.8	46.5	46.4
1,3-Dibrassidin (84)	—	63.5	66.5	58.8	68.5	63.1
1,3-Diolein (84)	—	18	—	—	25	39.7
1,3-Dielaidin (84)	—	49	53	49.8	55	52.6

	M.p., ° C.	Long spacing, Å.
1,3-Diolein (110)	21.5 ^a	39.3 ^a
1,3-Dilinolein (110)	— 2.6 ^a	45.2 ^a
1,3-Dilinolenin (110)	— 12.3 ^a	40.3 ^a

	β_1		β_2	
	M.p., ° C.	Long spacing, Å.	M.p., ° C.	Long spacing, Å.
1-Stearyl-3-olein (111)	52.0	48.2	—	39.0
1-Stearyl-3-elaidin (111)	65.9	52.6	62.0	50.0
1-Oleyl-3-elaidin (111)	28.8	48.4	—	—

^a Single polymorphic form.*(c) Diglycerides*

In the following discussion of the polymorphism of the individual glycerides the system of nomenclature introduced by Chen and Daubert is used (98). In this system the term "triacid-triglyceride" describes those triglycerides consisting of three different fatty acids. On this basis, symmetrical and unsymmetrical triglycerides containing two different fatty acids may be referred to as "diacid-triglycerides" and simple triglycerides as "monoacid-triglycerides."

This system differs from that used by Markley in this work and elsewhere, in that a glyceride containing only one kind of acid radical is

referred to generally as a homotriglyceride, and one with two or more different acid radicals as a heterotriglyceride or, if desired, dihetero- and trihetero-. Glycerides contain acyl radicals rather than acids, hence, according to Markley, it would be preferable to use as prefixes homo-acyl- and diheteroacyl- rather than monoacid- and diacid-.

The simple (monoacid) 1,3-diglycerides from didecain (C_{10}) to distearin (C_{18}) were investigated by Malkin *et al.* (105) who found three polymorphic modifications: (a) an α -form for which they were unable to obtain either x-ray long or short spacings; the alternation of the melting points, however, (Table 50) indicated to them that the α -modification crystallizes with the chains arranged vertically between terminal planes; (b) a β' -modification with an interesting discontinuity of melting points for the higher members; no β' -melting points above dimyristin being observed; (c) a β -modification which was observed for all members of the series.

Baur *et al.* (106) also investigated the diffraction of dilaurin, dimyristin, and distearin. They observed the heretofore missing melting points for the β' -form, indicating that there is no discontinuity in these data. They were unable to find any evidence for an α -modification with a short spacing of 4.2 Å. Howe and Malkin (107) re-examined the 1,3-diglycerides from didecain to distearin. Their results are given in Table 50. The values for the long spacings are in excellent agreement with those of Baur *et al.* (106), although the latter workers considered both modifications to be β -forms on the basis of a strong 4.6 Å. short spacing. They distinguished the two by designating them β -a and β -b, as first suggested by Malkin *et al.* (105). The two modifications can be distinguished by their short spacings, although there is not complete agreement as to the spacings characteristic of the different types.

Malkin *et al.* (105) first differentiated the two types as: "a"-type, short spacings 4.6 (S), 3.9 (S) and 3.73 (S); "b"-type, short spacings 4.6 (S), 3.9 (W), 3.73 (S) and 3.6 (W).

Baur *et al.* (106) proposed a classification, similar, but not identical: "a"-type, short spacings 4.6 (VS), 3.9 (M), and 3.7 (S); "b"-type, short spacings 4.6 (VS) and 3.75 (S).

Howe and Malkin (107) later proposed three types: "a"-type, β -form of odd acid glycerides and the β' -form of dipalmitin and distearin (Malkin *et al.* or Baur *et al.* type "a"); "b"-type, β' -form for all diglycerides except dipalmitin and distearin (Malkin *et al.* type "b"); "c"-type, β -form for all even acid diglycerides (Baur *et al.* type "b").

The b-type spacings, it was observed, are sometimes very similar to

TABLE 50
Melting Points and X-Ray Spacings of 1,2- and 1,3-Diglycerides

1,2-Diglyceride (107)	α			β		
	M.p., ° C.	Long spacing, A.	Short spacing, A.	M.p., ° C.	Long spacing, A.	Short spacing, A.
Dilaurin	20.0	39.2	4.13	39	34.1	4.31, 4.01, 3.79
Dimyristin	37.5	44.4	4.12	54	38.8	4.31, 4.06, 3.82
Dipalmitin	50.0	49.3	5.10	63.5	43.5	4.27, 4.03, 3.76
Distearin	54.5	54.5	4.12	71	48.3	4.27, 4.50, 3.81
1,3-Diglyceride (107)	β'			β		
Didecain	42	30.5	b ^a	44.5	32.5	c ^a
Diundecain	47	33.2	b ^a	49	35.2	a ^a
Dilaurin	54	35.7	b ^a	56.5	37.4	c ^a
Ditridecain	57	38.1	b ^a	59.5	40.4	a ^a
Dimyristin	63	40.5	b ^a	65.5	42.6	c ^a
Dipentadecain	66	42.5	b ^a	68.5	45.0	a ^a
Dipalmitin	71.5	44.7	a ^a	72.5	47.5	c ^a
Diheptadecain	72.5	47.7	b ^a	74.5	50.3	a ^a
Distearin	77	49.5	a ^a	78	52.8	c ^a
				β —Long spacing A.		
1-Myristyl-3-caproin (108)				38.0		
1-Palmityl-3-laurin (108)				42.7		
1-Stearyl-3-myristin (108)				47.6		

^a Short spacing type.

the α -type, but the latter are distinguished by the equal intensities of their three main lines.

In spite of some confusion in nomenclature, x-ray diffraction data, both long and short spacings, permit considerable differentiation of the various symmetrical diglycerides. Howe and Malkin (107) do not mention the α -modification of Malkin et al. (105) which Baur *et al.* do not believe exists. They show that their β' -form has a chain inclined at a tilt of $72^\circ 12'$, and their β -form a tilt of $66^\circ 30'$.

Howe and Malkin (107) published data on four 1,2-monoacid-diglycerides. Two solid forms were found, the metastable α - and the stable β -modifications. In contrast to the rapid $\alpha \rightarrow \beta$ -transition of 1,3-diglycerides, 1,2-diglycerides exhibited a very slow $\alpha \rightarrow \beta$ -transition. All of the 1,2-diglycerides crystallize in the double-chain length modification, the α -polymorph with a vertical chain and the β with a chain tilted at an

angle of 64° . X-ray diffraction and melting points for these diglycerides are included in Table 50.

Sidhu and Daubert (108) investigated three symmetrical diacid-diglycerides with the results shown in Table 50. All of their data fitted a single straight line, hence they considered all of them to represent the stable β -modification and used β -a and β -b to designate the two types observed.

Carter and Malkin (84) included four unsaturated monoacid-diglycerides in their investigations of simple glycerides of unsaturated acids (Table 49). Daubert and Sidhu (109) investigated the x-ray diffraction of 1,3-di-elaidin and obtained results which agreed very well with those of Carter and Malkin. They showed that slow crystallization invariably yields the β -form and that the β' -form is obtained by rapid crystallization from solvent. X-ray diffraction gave no evidence for the α -form.

Daubert and Lutton (110) published the results of measurements on 1,3-diolein, 1,3-dilinolein, and 1,3-dilinolenin and Benedict *et al.* (111) contributed data on three unsaturated diacid-diglycerides, namely, 1-stearyl-3-olein, 1-stearyl-3-elaidin, and 1-oleyl-3-elaidin (Table 49). The x-ray data for the monoacid-diglycerides of oleic, linoleic, and linolenic acids indicated a single polymorphic form for each glyceride which bore no relationship to any of the known glyceride structures. An unusual feature was that these three glycerides had a strong short spacing in the 4.7 Å. region, plus one additional strong line which was different in each case. No α -forms were found for any of the unsaturated diacid-diglycerides. 1-Oleyl-3-elaidin exhibits only one polymorphic form, and 1-stearyl-3-olein and 1-stearyl-3-elaidin, two forms. Both forms of the latter two glycerides apparently have the same short-type spacing, namely, β , and exhibit considerable individuality, but they do not fit into the β -a- and β -b-classification established for the saturated diglycerides. Benedict *et al.* (111) designated the stable form as β_1 and the unstable form as β_2 . X-ray diffraction and melting point data for several diglycerides of unsaturated acids are collected in Table 49.

(d) Monoacid (Simple) Triglycerides

The probability that the phenomenon of "double melting" or "triple melting" of triglycerides might be due to a type of polymorphism similar to that which had been established for the simple esters of the long-chain fatty acids was considered by Clarkson and Malkin (93). In order to relate the thermal behavior of these compounds with their polymorphic structures they resorted to x-ray diffraction, and thus initiated a study

which has clarified the thermal behavior of these compounds. They measured the x-ray diffraction of the monoacid-triglycerides from tricaprin (C_{10}) to tristearin (C_{18}) and found three polymorphic modifications as follows: (a) a lowest melting form, obtained by rapid cooling of the molten solid, which "is not truly crystalline, but possesses rather the characteristics of a glass," and which they called the vitreous form; (b) an unstable α -form obtained by holding the vitreous form slightly above its melting point; (c) the stable β -form obtained from transition of the α -form at room temperature.

The vitreous form exhibits no long spacings and only a single short spacing, a diffuse line at 4.2 Å., indicating to them that this form has a vertical rotating chain. The α -form crystallizes with vertical chains and exhibits, as expected, no alternation of melting points. The β -modification exhibits alternation of melting points throughout the homologous series, and has a chain inclined at an angle of 65° to the reflection planes. This tilt was later shown to vary for different groups of the triglycerides. The long spacing of the simple triglycerides is too long to correspond to the length of the acid radical, but it agrees with the reversed tuning fork arrangement postulated by Clarkson and Malkin (93), assuming two molecules between the terminal planes (Figure 11).

As mentioned earlier, three groups of workers (85–87) re-examined some of these monoacid-triglycerides and reported two important differences from the results reported by Clarkson and Malkin (93). None of these workers was able to find a vitreous form. Lutton (85) recommended that this term be dispensed with and Filer *et al.* (86) considered the data of Lutton as correcting faulty association of x-ray diffraction patterns with melting points by Clarkson and Malkin. All three of these groups also reported the detection of an additional polymorphic modification, β' , intermediate between the α - and β -forms. They presented both melting points and x-ray diffraction data for their three forms, i.e., α , β' , and β .

Clarkson and Malkin (89) reinvestigated the x-ray diffraction of the simple triglycerides and were able to verify the existence of the β' -form. They disagreed, however, with the advisability of eliminating the concept of a vitreous or glassy form. The data of Clarkson and Malkin (89) for the four forms, which they maintain do exist, are given in Table 51, together with values obtained by Lutton (85), which are in agreement with those of Filer *et al.* (86) and Bailey *et al.* (87).

(e) Diacid-Triglycerides

Four reports published by Malkin and his co-workers (112–115) describe investigations of the x-ray diffraction of diacid-triglycerides. The

TABLE 51
Melting Points and X-Ray Long Spacings of Monacid-triglycerides

Triglyceride	Vitreous	α	β'	β	α	β'	β
		<i>Melting points, ° C.</i>			<i>Long spacing, Å.^a</i>		
Trilaurin (85)	—	14	34	43.9	35.5	32.85	31.15
Trimyristin	—	32	44	55.5	41.4	37.65	35.45
Tripalmitin	—	44	55.5	65.5	46.3	42.3	40.9
Tristearin	—	54	64	73.1	50.6	46.8	45.15
Tridecylin (89,93)	-15.0	18.0	—	31.5	—	—	26.8
Triundecylin	1.0	26.5	29.0	30.5	33.0	29.5	29.6
Trilaurin	15.0	35.0	—	46.4	35.6	—	31.2
Tritridecylin	25.0	41.0	42.5	44.0	37.7	34.2	34.1
Trimyristin	33.0	46.5	54.5	57.0	41.2	37.6	35.8
Tripentadecylin	40.0	51.5	53.0	54.0	42.9	39.1	38.9
Tripalmitin	45.0	56.0	63.5	65.5	45.6	42.6	40.6
Trimargarin	50.0	61.0	62.5	64.0	48.5	43.7	43.5
Tristearin	54.5	65.0	70.0	72.0	50.6	47.2	45.0

^a The vitreous form does not exhibit long spacings.

pertinent data reported therein are summarized in Table 52. In all cases, four modifications of the diacid-triglycerides were found, namely, vitreous, α , β' , and β . Considerable individuality is manifested by the various diacid-triglycerides but certain similarities exist between members of the same group. Thus, in Table 52, groups A and B, from a report by Malkin and Meara (112), represent those diacid-triglycerides in which the 2-acyl radical contains two carbon atoms less than either of the 1,3-acyl radicals, and two carbon atoms more than either of the 1,3-acyl radicals, respectively. In both groups the vitreous form shows no long spacing and only the diffuse short spacing at 4.2 Å. All the α -modifications crystallize with a vertical chain and show a single short spacing at 4.19 Å. The two groups can be differentiated by the spacings of the β' - and β -modifications. The β' -modification has a vertical long chain and short spacings at 3.82 and 4.16 Å. in group A. In group B this modification crystallizes with an inclined chain tilted at an angle of $70^\circ 55'$ and has three strong short spacings at 3.85, 4.13, and 4.35 Å. The β -form is tilted at an angle of $69^\circ 33'$ for the diacid-triglycerides in group A and at an angle of $65^\circ 30'$ for those in group B. This form exhibits short spacings at 3.7, 3.8, 4.61, and 5.34 Å. in group A compared to 3.8, 4.0, 4.2, and 4.47 Å. for those glycerides in group B.

In group C, Table 52 (Carter and Malkin) (113), the 1-acyl radical contains two less carbons than either of the 2,3-acyls, and in group D it

TABLE 52

Melting Points and X-Ray Long Spacings of Diacid-triglycerides Investigated by Malkin and Co-workers

Diacid-triglyceride ^a	Vitreous	α	β'	β	α	β'	β
	<i>Melting points, ° C.</i>				<i>Long spacing, Å.^b</i>		
Group A: Symmetrical ^c							
2-Decyldilaurin	8	23	33	38.5	—	—	30.0
2-Lauryldimyristin	24	35	45	50	39.6	36.7	34.7
2-Myristyldipalmitin	37	46	55	60	44.4	42.4	39.0
2-Palmityldistearin	50	56	64	68	50.5	47.5	44.2
Group B: Symmetrical ^d							
2-Lauryldidecosin	6	25	34	37.5	—	—	29
2-Myristyldilaurin	24	37	44	48	—	34.5	33.6
2-Palmityldimyristin	38	49	55	58.5	45.0	39.7	38.1
2-Stearyldipalmitin	49	59	65	68	50.2	44.7	43.2
Group C: Unsymmetrical ^e							
1-Decyldilaurin	50	26	31	35.5	—	30.4	31.8
1-Lauryldimyristin	22	37	42	46.5	—	35.3	36.5
1-Myristyldipalmitin	36	47.5	52	57	43.9	40.3	41.5
1-Palmityldistearin	50	57	61	65	48.8	44.7	46.5
Group D: Unsymmetrical ^f							
1-Lauryldidecain	0	17.5	26	30	—	—	28.4
1-Myristyldilaurin	19	33.5	39	43.5	—	34.5	33.0
1-Palmityldimyristin	34	45.5	50.5	54	42.8	39.5	37.7
1-Stearyldipalmitin	46.5	55	59.5	62.5	47.8	43.9	42.5
Group E: Symmetrical ^g							
2-Decyldimyristin	16	37	40	43.5	—	33.7	52.5
2-Lauryldipalmitin	34	47	50	53.5	44.6	77.0	59.0
2-Myristyldistearin	47	56	59	62.5	49.5	44.7	65.8
Group F: Symmetrical ^h							
2-Myristyldidecain	3	21	30	34	—	30.3	46.5

^a Data for diacid-triglycerides, Groups A to L and "Unclassified," are summarized from the publications of Malkin et al. (112-115).

^b The vitreous form does not exhibit long spacings.

^c Group A: In each triglyceride the 2-acyl radical contains two less carbons than either of the pair of 1,3-acyls.

^d Group B: The 2-acyl radical contains two more carbons than either of the pair of 1,3-acyls.

^e Group C: The 1-acyl radical contains two less carbons than either of the pair of 2,3-acyls.

^f Group D: The 1-acyl radical contains two more carbons than either of the pair of 2,3-acyls.

^g Group E: The 2-acyl radical contains four less carbons than either of the pair of 1,3-acyls.

^h Group F: The 2-acyl radical contains four more carbons than either of the pair of 1,3-acyls.

TABLE 52 *Continued*

Diacid-triglyceride ^a	Vitreous	α	β'	β	α	β'	β
	<i>Melting points, ° C.</i>				<i>Long spacing, Å.^b</i>		
2-Palmityldilaurin	19	35	42.5	45.5	—	36.6	35.5
2-Stearyldimyristin	33	47	53	55.5	44.0	41.0	40.0
Group G: Symmetrical ⁱ							
2-Decyldipalmitin	20	42	48	51.6	39.0	74.0	56.5
2-Lauryldistearin	36	52	58	60.5	47.1	42.4	63.7
Group H: Symmetrical ^j							
2-Palmityldidecain	6	27	36	40	—	—	49.5
2-Stearyldilaurin	21	38	43	47	40.8	37.5	56.8
Group I: Unsymmetrical ^k							
1-Decyldimyristin	15	32	38	43.5	—	33.8	35.2
1-Lauryldipalmitin	32	45	49.5	54	43.4	38.5	39.8
1-Myristyldistearin	44	54	57.5	62	48.5	43.4	45.0
Group J: Unsymmetrical ^l							
1-Myristyldidecain	3	20	31	34.5	—	31.3	47.5
1-Palmityldilaurin	20	33	43	46.5	—	36.2	54.6
1-Stearyldimyristin	36	46	52	56	46.4	41.7	61.4
Group K: Unsymmetrical ^m							
1-Decyldipalmitin	23	37	41	45.5	—	74.1	56.2
1-Lauryldistearin	36	47	52	—	47.4	42.8	—
Group L: Unsymmetrical ⁿ							
1-Palmityldidecain	2	24	32	35	—	—	49.7
1-Stearyldilaurin	20	31	41.5	45	—	38.7	57.0
Unclassified:							
2-Stearyldidecain	5	34	40	44.5	—	—	51.6
2-Decyldistearin	30	47	53	57	—	76.3	61.2
1-Stearyldidecain	13	32	38	41	—	51.0	52.6
1-Decyldistearin	33	42.5	46	49	73.7	—	60.0

ⁱ Group G: The 2-acyl radical contains six less carbons than either of the pair of 1,3-acyls.

^j Group H: The 2-acyl radical contains six more carbons than either of the pair of 1,3-acyls.

^k Group I: The 1-acyl radical contains four less carbons than either of the pair of 2,3-acyls.

^l Group J: The 1-acyl radical contains four more carbons than either of the pair of 2,3-acyls.

^m Group K: The 1-acyl radical contains six less carbons than either of the pair of 2,3-acyls.

ⁿ Group L: The 1-acyl radical contains six more carbons than either of the pair of 2,3-acyls.

contains two more carbons than either of the 2,3-acyls. The short spacings are the same for each group: α , 4.19 Å.; β' , 3.83, 4.18, and 4.35 Å.; and β , 3.67, 3.86, 4.6, and 5.35 Å. The angle of tilt, however, shows a variation. The α -modification is vertical in both groups; for β' it is inclined at angles of $68^\circ 6'$ and $63^\circ 30'$ for groups C and D, respectively; and for β it is inclined 73° and 62° , respectively, for the two groups.

In groups E, F, G, and H from Malkin and Meara (114), the differences in lengths of the fatty acids is somewhat greater, as indicated in Table 52. Malkin and Meara noticed that the long spacing is too long for a single molecule between successive reflecting planes, and too short for a double molecule without an acute tilt. This difficulty was later explained by Lutton's triple chain-length structure (94) (Figure 11). The short spacings for these groups are very similar: α , 5.2 to 5.3 Å.; β' , 3.8 to 3.9, 4.1, and 4.3 to 4.4 Å.; and β 4.6, 3.8, 4.1, and 4.3 Å. Angle of tilt was given, for the β -form in group E only, as $41^\circ 18'$.

The compounds listed under I, J, K, and L from a report by Carter and Malkin (115) concluded the investigation of Malkin and co-workers on these diacid-triglycerides. All members of these groups crystallize in forms corresponding to twice the length of a single molecule and all reveal the same short spacings: α , 4.19 Å.; β' , 3.8, 4.1, and 4.3 Å.; and β , 3.8, 4.2, 4.8, and 5.2 Å. For the β' - and β -forms of groups I and J, the angles of tilt were given for β' and β in group I as $75^\circ 45'$; and in group J, β' vertical and β , as $43^\circ 45'$. From their studies Malkin and associates concluded that melting points of the various groups are so close that differentiation by this characteristic is almost impossible. Two types can readily be distinguished by their x-ray data. For the identification of a diacid-triglyceride from a natural product neither x-ray diffraction nor capillary melting-point methods alone are wholly conclusive, but used in conjunction they offer a high probability of correct identification.

Lutton *et al.* (88) and Lutton and Jackson (116) reinvestigated the x-ray diffraction of the four mixed triglycerides of palmitic and stearic acids, namely, 2-palmityldistearin, 2-stearyldipalmitin, 1-palmityldistearin, and 1-stearyldimyristin (88), and of 1-myristyldistearin, 1-myristyldipalmitin, 1-stearyldimyristin and 1-palmityldimyristin (116). They found that all of these triglycerides are more striking in their individuality than in their similarity. The 2-palmityldistearin was unique in that the α -form was unusually stable, while for the 2-stearyldipalmitin it was unstable. Both of these glycerides exist in only one form other than the α . The 2-palmityldistearin was normal in that the β -form was the most

stable, but the 2-stearyldipalmitin manifested a most stable β' -form. The 1-palmityldistearin and 1-stearyldipalmitin exhibited three forms, α and β' , obtained from a melt, and β , obtained only from solvent. Lutton *et al.* (88) showed that their data, summarized in Table 52a, differed from that of Malkin and co-workers in several important details as follows:

1. No glassy form was found, the α -form is actually the lowest melting form.

2. The number of forms never exceeds three. In two cases, where Malkin *et al.* report four, only two were found.

3. The stable form of 2-stearyldipalmitin is the β' -modification, not the β -form, as stated by Malkin *et al.*

4. The 2-stearyldipalmitin is reported as impossible of achieving a complete melting point for the α -form as the softening point is 3° below the melting point reported by Malkin.

5. The 2-palmityldistearin exhibits no β' -form.

All of these triglycerides, according to Lutton and co-workers, exhibit a lowest melting point α -form, unusually stable in the case of 2-palmityldistearin and unusually labile in the case of 2-stearyldipalmitin. The forms other than the α -modification for each of these triglycerides are: 2-palmityldistearin, only β ; 2-stearyldipalmitin, only β' ; 1-palmityldistearin, β' from melt and β from solution, both equally stable; 1-stearyldipalmitin, β' and β , the latter the stable form.

Jackson and Lutton (116) found that the polymorphism of 1-myristyldistearin, 1-myristyldipalmitin, 1-stearyldimyristin, and 1-palmityldimyristin was even more complex than that of the triglycerides of the first-mentioned group. These latter crystallize in various chain-length modifications as shown in Table 52a. 2-Myristyldistearin exhibits both a β' -4, as well as a β' -2-form. The β' -4-form was not reported by Malkin and Meara (114). In a discussion of multiplicity of chain lengths, Lutton (94) stated that 1-stearyldilaurin also crystallizes in a β' -4-modification.

Diacid-triglycerides with greater differences in chain length between the acyl groups were investigated by Jackson *et al.* (97) (Table 52a). A most striking characteristic of this group is that no member of it exhibits a β' -modification. The 2-acetyldistearin and 2-acetyldipalmitin exhibit only sub- α - and β -3-modifications. The 2-butyryldistearin, 2-butyryldipalmitin, 2-caproyldistearin and 2-caproyldipalmitin exhibit, besides the β -3-form, three α -forms, namely, sub- α -1, α -1, and super- α -1. All of these α -forms, except the sub- α -3 of the 2-caproyldipalmitin, crystallize with a single molecule between reflecting planes, which necessitated postulating a single chain-length structure for mixed triglycerides with

chains of markedly different lengths (Fig. 11). The super- α -forms of 2-butyryldistearin and 2-butyryldipalmitin are unique for triglycerides. The designation of the form derives from the single short spacing at 4.4 Å. and a melting point 10° to 12° higher than that of the α -modification.

Jackson and Lutton (95) concluded that "where chain length difference of 2 or less occur within triglycerides, it is typical to observe three polymorphic forms, α , β' , and β , each of double-chain-length structure. With greater chain length difference there are many and varied exceptions to this behavior." They investigated the x-ray diffraction of 1-stearyl-diacetin, 1-stearyldibutylin, 1-stearyldicaprin, 1-palmitoyldiacetin, 1-palmitoyldibutylin, 1-palmitoyldicaprin, and 1-stearyldipropionin (Table 52a). All of these triglycerides exist in triple chain-length structures. Only the 1-stearyldicaprin and 1-palmitoyldicaprin exist in a β' -form and these two exhibit no true α -form. The 1-stearyldicaprin exhibits a β -form while the 1-palmitoyldicaprin does not.

Jackson and Lutton (117) also measured the spacings of four diacid-triglycerides, namely, 2-behenyldipalmitin, 2-behenyldistearin, 1-palmitoyldibehenin and 1-stearyldibehenin (Table 52a). All of these compounds crystallize in the highly stable β' -a-form. The 1-palmitoyldibehenin actually manifests no β -form. The 2-behenyldipalmitin and 2-behenyldistearin crystallize in the β -3-modification, but 1-stearyldibehenin crystallizes in the β -2-form. The α - and β -forms exhibit typical double chain-length structures. Of particular interest was the discovery of a new sub- α -form of these compounds. This form seems to exist for the unsymmetrical behenyl glycerides at low temperatures. At higher temperatures it is reversibly transformed to the α -modification. It appears to be analogous to the sub- α -form of monoglycerides and may be characteristic of unsymmetrical triacid-triglycerides.

(f) Triacid-Triglycerides

Chen and Daubert (119) and Filer *et al.* (118) obtained the melting points and x-ray diffraction spacings of twelve triacid-triglycerides as shown in Table 53.

The β' -form of these triglycerides is obtained by rapid crystal growth from solution, and the β -form by slow crystal growth. The β' -long spacing agrees with that for the form previously designated, from melting-point data, form I, and the β -long spacing with that for the older form II, but the short spacings do not agree with a β - and β' -classification. Sidhu

TABLE 52a. Melting Points and X-ray Long Spacings of Diacid-triglycerides Investigated by Lutton and Co-workers^a

Diacid-triglyceride ^b	α -2	Sub- α -2	β' -2	β' -3	β' -4	β -2	β -3
2-Palmyldistearin	49.2 (51.8)	—	—	—	—	—	43.1 (68.5)
1-Palmyldistearin	48.5 (50.6)	—	45.1 (65.0)	—	—	—	44.7 (65.2)
2-Stearyl dipalmitin	46.65	—	42.75 (68.6)	—	—	—	—
1-Stearyl dipalmitin	47.6 (47.4)	—	43.8 (61.7)	—	—	—	42.1 (62.7)
2-Myristyldistearin	47.6 (44.2)	—	43.7 (56.6)	—	85.0 (59.3)	—	66.3 (63.8)
2-Myristyldipalmitin	44.6 (40.1)	—	43.3 (47.0)	—	—	39.2 (60.3)	—
1-Stearyl dimyristin	44.5 (35.9)	—	—	41.3 (46.5)	—	37.5 (54.4)	61.7 (56.4)
1-Palmyldimyristin	43.1 (35.6)	—	38.9 (46.5)	—	—	—	—
2-Behenyldipalmitin	50.0 (47.4)	—	46.0 (61.5)	—	—	—	70.4 (66.6)
2-Behenyldistearin	53.2 (56.0)	—	49.4 (64.0)	—	—	—	75.1 (70.6)
1-Palmyldibehenin	57.4 (55.9)	58.9	52.4 (66.1)	—	—	54.6 (73.5)	—
1-Stearyl dibehenin	59.1 (61.3)	61.4	53.3 (71.5)	—	—	—	—
	Sub- α -3		α -3	β' -3			β -3
1-Stearyl diacetin	37.1	36.5 (34.1)	—	—	—	—	34.0 (47.8)
1-Palmyldiacetin	34.7	34.1 (22.4)	—	—	—	—	31.5 (42.3)
1-Stearyl dipropionin	40.5	39.5 (23.5)	—	—	—	—	34.1 (31.7)
1-Stearyl dibutyryl	42.1	42.3 (15.6)	—	—	—	—	—
1-Palmyldibutyryl	39.9	39.6 (2.9)	—	—	—	—	—
1-Stearyl dicaproin	45.5 (6.0)	—	—	41.2 (16.9)	—	—	38.3 (21.2)
1-Palmyldicaproin	43.2 (-7.4)	—	—	39.7 (12.0)	—	—	—
	Sub- α -1	α -1	Super- α -1	Sub-A- β -3	Sub-B- β -3		β -3
2-Acetyldistearin	28.2 (40.4)	—	—	—	—	—	52.1 (62.8)
2-Acetyldipalmitin	25.7 (28.4)	—	—	—	—	—	47.2 (54.8)
2-Butyryldistearin	29.8	28.5 (33.4)	26.6 (42.7)	—	—	—	48.4 (54.8)
2-Butyryldipalmitin	26.9	25.9 (20.6)	24.2 (32.6)	—	—	—	45.0 (46.5)
2-Caproyldistearin	30.4	30.0 (27.7)	—	55.6 (46)	54.5 (46.0)	—	56.8 (53.1)
2-Caproyldipalmitin	53.7 (13.4)	—	—	52.8 (40.5)	49.2 (40.5)	—	52.5 (44.5)

^a The data in this table are summarized from the publications of Lutton and co-workers (88,95,97,116,117).^b Throughout this table the first figure is the spacing value in Å. and is followed by the melting point in °C. in parentheses.

TABLE 53

Melting Points and X-Ray Long Spacings of Triacid-triglycerides (118-120)

Triacid-triglyceride	β' -Form	β -Form	β' -Form	β -Form
	<i>Melting points, ° C.</i>		<i>Long spacing, Å.</i>	
1-Stearyl-2-myristyl-3-palmitin	56.1	59.5	41.5	63.4
1-Stearyl-2-lauryl-3-palmitin	56.0	57.5	—	61.2
1-Stearyl-2-capryl-3-palmitin	53.8	55.0	—	60.0
1-Stearyl-2-palmityl-3-myristin	56.0	58.5	—	40.5
1-Stearyl-2-lauryl-3-myristin	51.9	55.0	—	59.8
1-Stearyl-2-capryl-3-myristin	50.1	52.5	—	57.3
1-Stearyl-2-palmityl-3-laurin	47.0	52.0	43.3	62.4
1-Stearyl-2-myristyl-3-laurin	45.5	49.5	40.1	59.6
1-Stearyl-2-capryl-3-laurin	—	41.8	—	54.9
1-Stearyl-2-palmityl-3-caprin	46.5	50.0	59.0	38.5
1-Stearyl-2-myristyl-3-caprin	42.0	45.0	54.3	56.1
1-Stearyl-2-lauryl-3-caprin	40.0	44.0	53.0	35.6
1-Stearyl-2-palmityl-3-myristin	—	—	—	40.7
1-Palmityl-2-myristyl-3-laurin	—	—	—	35.7
1-Myristyl-2-lauryl-3-caprin	—	—	33.4	—

and Daubert (120) later studied the x-ray diffraction of 1-stearyl-2-palmityl-3-myristin, 1-palmityl-2-myristyl-3-laurin, and 1-myristyl-2-lauryl-3-caprin (Table 53). They found that the 1-myristyl-2-lauryl-3-caprin crystallizes from solution, either rapidly or slowly, in a β' -form. However, in general, for these triacid-triglycerides there were sufficient differences in short spacings to indicate some uncertainty in designating the form on the basis of short-spacing classification.

(g) Unsaturated Triglycerides

Data obtained by Lutton and co-workers (121-123) in a series of investigations of triolein and of diacid- and triacid-triglycerides of oleic acid with palmitic and stearic acids are collected in Table 54.

Wheeler *et al.* (124) obtained evidence from the thermal behavior of triolein that it could exist in three polymorphic forms melting at -32° , -13° , and 5.5° C. The existence of these polymorphic forms was confirmed by x-ray examination by Ferguson and Lutton (121) which revealed the α -, β' -, and β -modifications, all with the double chain-length structures. Monoacid-(simple) triglycerides of unsaturated acids have the same polymorphic forms as the saturated simple triglycerides. The long spacings for triolein (Table 54) are slightly shorter than the corresponding spacings for tristearin; and the spacing of the α -modification

TABLE 54
Melting Points and X-Ray Long Spacings of Oleyl-diacylglycerides^a

Unsaturated triglyceride	α -2		α -3	Sub- β -2	β' -2	Sub- β -3	β -3
2-Oleyldistearin (122) (synthetic)	—		80.9 (22.4)	—	—	71.8 (36.2)	64.8 (44.3)
2-Oleyldistearin (natural)	—		80.4 (23.0)	—	—	72.9 (37.0)	64.1 (42.0)
2-Oleyldipalmitin (123)	45.7 (18.1)		—	42.6 (26.5)	42.5 (33.5)	—	60.9 (38.3)
	Vitreous	α	β''	β'	β		
2-Oleyldimyristin (125)				39.1 (26.5)	56.7 (28.5)		
2-Oleyldipalmitin	(2.0)	(11)	(19.0)	68.5 (29.0)	42.1 (35.0)	60.7 (37.5)	
2-Oleyldistearin		50.3 (23.0)	72.5 (37.0)	45.2 (41.5)	64.8 (43.5)		
		Sub- α -3, Sub- α -3, α -3 A B				β' -3	β -3
1-Oleyldistearin (96)	80 (30.4)	84 (>0)	82 (20)			70.8 (43.5)	— (42.5)
1-Oleyldipalmitin	77.6 (18.5)	—	—			65.3 (35.2)	— (34.8)
	α -2	Sub- α -2	Sub- α -3	Sub- β' -3	β' -2	β' -3	β -3
1-Palmityl-2-oleyl-3-stearin	47.8 (18.2)	—	75 (>5)	—	44	66.8 (33)	63.1 (37.3)
1-Oleyl-2-palmityl-3-stearin	40.3 (25.3)	40.3 (>0)	—	68.5 (37.0)	—	66.9 (40.2)	—
1-Oleyl-2-stearyl-3-palmitin	—	40.6 (26.3)	77 (>20)	—	43.6 (40.2)	67.6 (39.8)	—
	α -2				β' -2	β -2	
Triolein (121)	45.2 (-32)				45.8 (-13)	43.3 (5.5)	

^a The first figure refers to long spacing in Å., followed by melting point in °C. in parentheses.

is short enough to suggest a tilted structure which would be unusual for an α -form.

Three polymorphic forms were observed for 2-oleyldistearin (122). The forms with the lowest and the highest melting points were readily classified by means of their short spacings (see Table 44) as the α - and the β -

modifications. The intermediate form does not agree with a β' -classification from short spacing data and was therefore designated X-form. It was also suggested that it be designated β'' but was later classified as a sub β -3-form (123). No evidence was found for the existence of a proposed (125) fourth modification with a melting point about 30° C. and Lutton (122) maintained that, if such a form does occur, its existence is very transitory.

The long spacings of 2-oleyldistearin are different from those of tristearin and they exhibit different patterns of intensities of successive orders of reflection. Lutton (122) proposed the triple chain-length structure (Fig. 11) to account for the magnitude of the long spacings. A single chain-length structure exhibits a gradual decline of intensities with increasing order of reflection, while a double chain-length structure shows an alternation between odd and even carbon-chain members. These triple chain-length structures, however, exhibit intense lines for the 5th, 8th, and 10th orders. From a consideration of Shearer's (40) explanation for the alternation of intensities, Lutton demonstrated how a triple chain-length structure would result in such a pattern.

The 2-oleyldistearin can be differentiated from the 2-oleyldipalmitin because the latter has two intermediate forms, namely, the double chain-length structure, corresponding to sub β -2 and β' -2 (123), while the only intermediate form observed for the first-mentioned is one corresponding to the triple chain-length β -3-form.

Malkin and Wilson (125) published data on these two compounds together with those for 2-oleyldimyristin. They found five forms, glassy or vitreous, α , β'' , β' , and β . They agreed with Lutton's proposed triple chain-length structure but disagreed as to the number of modifications. From examination of the data obtained by both groups of workers, Malkin concluded, "it seems probable that Dr. Lutton's failure to observe forms reported by other workers is due to the rapidity with which his heating curves are taken, since this tends to smooth out details."

Lutton and Jackson contend that no vitreous or β'' -forms of 2-oleyldipalmitin could be found despite a careful search for them. They suggested that Malkin's β' is equivalent to their sub- β' except that the melting point is 8–9° higher, indicating confusion with the β' -2-form. Except for the number of observed forms, the data of Lutton and of Malkin agree rather well, and the only major disagreement pertains to the long spacing of the α -form of 2-oleyldistearin. For this form Malkin reported a single chain-length structure with a long spacing of 50.3 Å.,

whereas Lutton assumed it to have a triple chain-length structure with a long spacing of 80 Å. (Table 54).

Filer *et al.* (86) also reported x-ray diffraction data for 2-oleyldistearin, 2-oleyldipalmitin, and 2-oleyldimyristin. They found long spacings corresponding to a sextuple chain-length structure required by a $1\frac{1}{2}$ order, which made it necessary to double the long spacings. This order was not observed by Lutton (122) and he believes that the long spacings of Filer *et al.* are twice the correct values.

Lutton (96) also measured the x-ray spacings of the two diacid-triglycerides, namely, 1-oleyldistearin, and 1-oleyldipalmitin; and the three triacid-triglycerides, namely, 1-palmityl-2-oleyl-3-stearin, 1-oleyl-2-palmityl-3-stearin, and 1-oleyl-2-stearyl-palmitin. The 1-oleyldistearin and 1-oleyldipalmitin exist in two forms, both with the triple chain-length structure of the "chair-type" (Fig. 11a), and are classified as α and β' on the basis of their short spacings (Table 54). The 1-oleyldistearin has, in addition, a sub- α -form stable to 20° but showing a modification at 0° C. The 2-oleyl compound, 1-palmityl-2-oleyl-3-stearin, has a stable triple chain-length structure, β -3, but all the 1-oleyl compounds have a stable β' -form. When crystallized from solvent, these compounds appear in the β' -3-modification. When obtained from a melt, 1-oleyldistearin and 1-oleyldipalmitin also crystallize in the β' -3-form, but 1-oleyl-2-palmityl-3-stearin has the sub- β' -3-form when obtained from a melt, and 1-oleyl-2-stearyl-3-palmitin has the β' -2-form (Table 54).

Lutton concluded that "It has not been possible up to this time (1951) to develop a single system to account for all the diverse polymorphic behavior of these glycerides." However, "Because of the considerable degree of individuality it should be possible to use the information now available to establish in many cases the identity of predominant oleyl-disaturated glycerides in such fats as lard, cacao butter and tallow."

Melting points and x-ray spacings of two monoacid- and ten diacid-triglycerides containing elaidic or petroselaidic and palmitic or stearic acids have been published by Minor and Lutton (126) and by Malkin and Wilson (125). These data are collected in Table 54a. Minor and Lutton were unable to find the vitreous form reported for these compounds by Malkin and Wilson. All of the elaidyl and petroselaidyl glycerides show double chain-length structures in each form. Thus, they resemble tristearin and are unlike the oleyl glycerides which commonly show triple chain-length structures, as well as other polymorphic complications. According to Lutton, "this difference shows the greater tendency of oleyl

chains to segregate, or alternatively the greater compatibility of elaidyl or petroselaidyl with saturated chains."

TABLE 54a

Melting Points and X-ray Long Spacings of Elaidyl- and Petroselaidyl-triglycerides^a

Unsaturated triglyceride ^b	Vitreous	α	β'	β
Trielaidin	—	49.6 (15.3)	—	44.6 (42.4)
1-Palmityldielaidin	—	48.8 (22.8)	44.3 (33)	44.1 (40.3)
1-Stearyldielaidin	—	50.5 (28.8)	—	44.75 (49.6)
2-Elaidyldipalmitin	—	45.5 (36.8)	43.0 (53.2)	42.05 (53.3)
2-Elaidyldistearin	—	50.8 (42.9)	46.9 (47)	45.0 (59.5)
2-Palmityldielaidin	—	48.6 (26.0)	44.1 (32.0)	43.2 (44.5)
2-Stearyldielaidin	—	48.7 (34.0)	45.9 (43.2)	44.8 (50.1)
Tripetroselaidin	—	49.5 (18.8)	—	44.6 (52.5)
1-Palmityldipetroselaidin	—	48.9 (26.4)	45.3 (35.9)	43.4 (46.4)
1-Stearyldipetroselaidin	—	50.5 (31.5)	—	44.6 (55.0)
2-Petroselaidyldipalmitin	—	47.5 (35.9)	42.7 (54.3)	41.7 (54.9)
2-Petroselaidyldistearin	—	50.8 (43.4)	—	44.8 (62.6)
2-Elaidyldipalmitin (125)	— (33.0)	— (42.0)	44.7 (52.5)	42.7 (55.0)
2-Elaidyldistearin (125)	— (40)	51.2 (46)	47.2 (58.0)	44.9 (61.0)

^a The first figure refers to long spacing in Å, followed by melting point in °C. in parentheses.

^b Data for all except last two compounds are from Minor and Lutton (126).

(h) Reviews and Summary of the Polymorphism of Glycerides

The application of x-ray diffraction to the solution of the complex problem of the polymorphic behavior of glycerides, including the identification of the various crystalline forms of these substances, has been the subject of several reviews. These articles cover, in a general way, the accumulated knowledge of this subject through 1954, including the method of use, advantages, and limitations of the application of x-ray diffraction and thermal techniques to the resolution of important problems of crystal structure of glycerides. Some of the authors have devoted considerable space toward resolving the conflicting views of several schools regarding the interpretation of x-ray diffraction and melting point data as they apply to the polymorphic structure of the various crystalline forms of glycerides.

One of the early reviews was published by Ferguson and Lutton (52) in 1941. In 1950, Lutton (90) summarized his views on the controversial interpretation of x-ray diffraction and related data and information with reference to various polymorphic types of glycerides. Still later (1955), Lutton (127) discussed the application of x-ray diffraction to studies of

polymorphism of glycerides, particularly as it applies in the cosmetic field.

Malkin (92,128) published two reviews setting forth his views and recommendations on the subject and recapitulated the points of disagreement with other workers in this field. Other reviews which the reader may wish to consult have been published by Daubert (129), Daubert and King (129a), and Bailey (129b).

7. Applications of X-Ray Diffraction to Problems in Fatty Acid Chemistry

The contributions which the application of x-ray diffraction has made toward understanding the polymorphic phenomena exhibited by glycerides, have overshadowed its other applications in the field of fatty acids during the past quarter of a century. However, applications of x-ray diffraction, based on the principles established by the early work of Müller, Schearer, Piper, and others, have been applied with increasing frequency to the solution of practical problems in this field. As an analytical tool, x-ray diffraction has found an important place in several fields of research on fatty acids and their derivatives.

In a review of x-ray spectroscopy, Singleton (130) emphasized the economic importance of polymorphism and cited several applications of the use of x-ray diffraction for the identification of polymorphic forms. Hellman *et al.* (131) found x-ray diffraction useful in following changes in consistency during tempering of so-called "global spreads." Throughout the tempering there was no evidence that any polymorphic transformation of the monoglyceride components of the products had occurred. However, there was an increased sharpness of the diffraction lines, indicating an increase in perfection or size of the crystals, without alteration of crystal structure. The same workers (132) later showed that decreased solubility of the tempered samples is related to increased crystallinity, as determined by x-ray diffraction. This increased crystallinity was presumed to be a dominant factor in causing softening on tempering, and possibly was responsible for increased flow properties which contribute to better mouthing qualities of the "global spread."

The remarkably enhanced baking characteristics of rearranged, as compared to ordinary, lard cannot be related to changes in iodine value, saponification value, total fatty-acid composition, etc., but Hoerr and Waugh (133) observed that the x-ray diffraction patterns were generally more diffuse in rearranged than in ordinary lard, indicating that the former fat possesses a less well-ordered arrangement of its molecules than the latter. Rearrangement of the lard did not affect the nature of the short

spacings but produced an increase in the long spacing from 39 to 48 Å. Figure 12 illustrates how x-ray diffraction patterns can be applied to demonstrate the changes occurring in crystal structure as a result of rearrangement, and to differentiate ordinary from rearranged lard.

Teeter *et al.* (134) identified the carbonyl components present in the volatile "beany," distillate fraction from soybeans by means of x-ray diffraction patterns of the 2,4-dinitrophenylhydrazones of these compounds. Singleton *et al.* (135) used x-ray diffraction to study the polymorphism of α - and β -tung oils. Polymorphism was not observed in α -tung oil, but three polymorphic forms of β -tung oil were distinguished. Singleton *et al.* (136) employed x-ray diffraction to identify the polymorphic forms of stearic acid used in dilatometric and thermal measurements. They found that the B-form of this acid could be obtained most

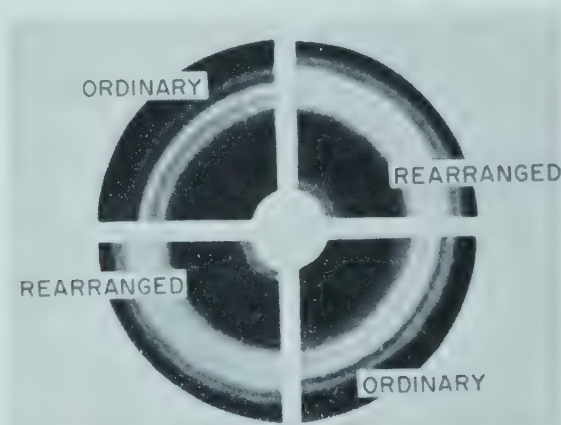


Fig. 12. X-ray diffraction patterns of fats tempered for about 2 weeks at 25° C. (133).

readily by slow crystallization from benzene at room temperature, and the C-form by crystallization from hot glacial acetic acid. The two forms were identified by their characteristic x-ray spacings. Similarly, Ward and Singleton (137) resorted to x-ray diffraction to identify and check the purity of polymorphic forms of palmitic acid used in investigations of dilatometric and thermal properties.

Witnauer *et al.* (138) showed that x-ray diffraction can be applied for the quantitative analysis of binary mixtures of *trans,trans*-9,11- and *trans,trans*-10,12-linoleic acids. If, in such mixtures, the concentration of the 10,12-component is not less than 25% or the 9,11-isomer is not less than 5%, the x-ray pattern will show the presence of each component. By use of solidification points and x-ray-spacing data, the composition of a mixture of these acids can be established to within $\pm 3\%$. X-ray spacings

of the *trans*-octadecenoic acids from C₆ through C₁₂ have been reported by Swern *et al.* (139). They also reported diffraction data for the two dihydroxystearic acid derivatives of these compounds and for 50:50 binary mixtures of these three groups of compounds.

The x-ray diffraction data for the synthetic enantiomeric α -lecithins have been reported by Baer *et al.* (140) and by Baer and Kates (141). Bevans and Malkin (142) reported x-ray data for synthetic $\pm\alpha$ - and β -cephalins. Gregory and Malkin (142a) and Egerton *et al.* (143) applied x-ray diffraction methods to investigations of sphingolipids. Gupta and Malkin (144) published x-ray diffraction data for chaulmoogric (13-cyclopent-2'-enyl-*n*-tridecanoic) and hydnocarpic (11-cyclopent-2'-enyl-*n*-undecanoic) acids and for their mono-, di-, and triglycerides. Trillat and co-workers investigated the x-ray diffraction of numerous long-chain organic compounds, including higher symmetrical ethers (145), diketones, acryloins, and glycols (146), and recommended the method for following the purification of such compounds or for the rapid determination of the total number of carbon atoms. By means of x-ray diffraction analyses of the product of chromic acid oxidation of corynomycolic acid of diphtheria bacilli, $(\pm)$ -1-tetradecyl-2-hydroxystearic acid, C₁₅H₁₃-CH(OH)CH(C₁₄H₂₉)COOH, was identified by Lederer *et al.* (147) as palmitone. Similar oxidation of the methyl ester yields methyl- α -palmitoylpalmitate.

Stosick (148,149) investigated the x-ray diffraction of solid soap and concluded that the bulk of x-ray diffraction patterns obtained with powder samples of soap, i.e., with those samples for which no special efforts were made to obtain good crystal growth, can be interpreted as the random interposition of micellar layers. Most of the lines which have been called short spacings or side spacings are merely high orders of the 001 series. "It is clear that any attempt to use such power diagrams in phase studies of the soaps is, at best, beset with gravest uncertainties. A sample of unchanging composition might give a great range of distinguishably different diffraction patterns corresponding to varying degrees of order." X-ray diffraction was found very useful by Marsel and co-workers (150) in the detection of additives in vegetable waxes.

X-ray diffraction and melting point data for isomeric 9,10-epoxy- and 9,10-dihydroxystearic acids, and for 9,10-epoxyoctadecanols have been published by Witnauer and Swern (151). They found that each member of an isomeric pair can be identified readily and positively by the position and intensity of the x-ray diffraction lines. Powder patterns of binary mixtures of the isomeric 9,10-dihydroxystearic acids show characteristic

lines even when present in as little as 1% of the mixture and the composition of such binary mixtures can be determined to $\pm 3\%$ by the relative intensities of the diffraction lines. On the basis of their characteristic short spacings, Vicknair *et al.* (152) showed that 1,2-diaceto-3-stearin and 1-aceto-2,3-stearin exist in three polymorphic forms, namely, α , sub- α , and β . O'Connor *et al.* (153) obtained x-ray diffraction patterns for 10-hydroxystearic and 12-hydroxystearic acids, which exhibit considerably different gelling properties, and showed how the two could be distinguished by their characteristic short spacings. X-ray diffraction patterns were also used by O'Connor and co-workers to characterize molecular compounds of acetamide and long-chain saturated fatty acids. By means of its long spacings any of these compounds could be identified (154).

Subsequent to about 1945 a considerable amount of x-ray diffraction data for fatty acids and derivatives thereof have been published from the University of Uppsala. These investigations may be divided into three types or groups as follows: (1) investigations, mostly by Erik von Sydow, on the complete crystal analysis of several fatty acids; (2) use of x-ray diffraction powder patterns for the characterization of certain fatty acids and their simple derivatives prepared by Einar Stenhagen and his co-workers; and (3) x-ray data on some optically active higher aliphatic compounds by Stina Stållberg-Stenhagen and co-workers.

The contributions of von Sydow on the crystallographic analysis of fatty acids are included in the next section. Einar Stenhagen and co-workers have used x-ray diffraction powder patterns to characterize a considerable number of normal and branched-chain aliphatic acids and such derivatives thereof as the 2-keto acids and esters, iso-2-keto acids, esters and alcohols, and iso-acid amides.

Stenhagen (155), and subsequently von Sydow and Stenhagen (156), applied an x-ray camera designed for continuous recording of diffraction pattern-temperature diagrams in one of the most exhaustive investigations of the phase transitions between 30° C. and the melting point of the normal aliphatic monocarboxylic acids with 12 to 29 carbon atoms. Their data, which are collected in Table 55, also include measurements on several compounds not previously published. Where earlier values were available, Stenhagen and von Sydow included them in their tabulations for purposes of comparison.

In agreement with Francis *et al.* (58), the even-numbered carbon acids were found to crystallize in the C-form on slow cooling of the melt. The odd-numbered carbon acids under these conditions were obtained in the B-form, in agreement with Francis and Piper (56). An A-form for the

TABLE 55
Polymorphism of Saturated Long-chain *n*-Aliphatic Acids (156)

Carbon atoms	M.p., ° C.	Long spacing, A.			Transition on heating, ° C.			Crystal form ^a from		
		A	B	C	A to C	B to C	Glacial acetic acid	Light petro- leum	Mel	
<i>Even series</i>										
12	44.0	32.1	—	27.4	32	—	C	A	C	
14	54.2	36.7	—	31.7	44	—	C	A	C	
16	62.9	41.7	—	36.0	59	—	C	A	C	
18	69.7	46.5	44.1	40.0	54	46	A + C	B + C	C	
20	75.1	—	48.8	43.9	—	52	B + C	B + C	C	
22	79.9	55.5	—	48.3	63	—		A + C ^b	C	
24	83.9	—	57.8	52.9	—	65		B + C	C	
26	87.5	—	62.2	57.1	—	72		B + C	C	
28	90.7	—	67.5	61.6	—	79		B	C	
		A'	B'	C'	A' to C'	A' to B'	B' to C'			
<i>Odd series</i>										
13	41.4	35.1	—	29.6	34	—	A'	A'	A'	
15	52.1	40.2	36.4	34.5	—	45	A' + B'	A'	B'	
17	61.1	—	40.3	38.5	—	56	B'	B'	B'	
19	68.5	49.2	44.7	43.0	—	52	B'	B'	B'	
21	74.8	—	49.1	46.9	—	72		B'	B'	
23	79.1	—	53.6	51.0	—	77.5		B'	B'	
25	83.2	—	58.0	56.2	—	81.5		B'	B'	
27	87.5	—	62.7	60.0	—	85		B'	B'	
29	90.4	—	66.6	65.2	—	89		B'	B'	

^a Letters designate the crystal form of the acid obtained on crystallization at 30° C. from different solvents.

^b Crystallized from benzene.

C₁₂- and C₂₂-acids and an A'-form for the C₁₉-acid were reported. The C₂₇-acid, not previously reported, was found to exist in a B'-form at lower temperatures, changing to the C-form near the melting point. Values for the C'-spacings of the C₂₃-, C₂₅-, C₂₇-, and C₂₉-acids were reported for the first time. No D'-form of the odd-carbon acids (55) was observed. All odd-numbered carbon acids with 15 or more carbon atoms showed a reversible B' to C'-transition. The C₁₃-acid showed a reversible A' to C'-transition and the C₁₅- and C₁₉-acids when obtained in the A'-form on heating, first underwent an A' to B'-transition. For the even-numbered carbon acids the C-form appeared to be the stable form as the

transitions A to C and B to C were not reversible. No A to B-transition was observed. The crystalline forms obtained by Stenhagen and von Sydow (156) from various solvents at a temperature of 30° C. are included in Table 55. For more complete data on the polymorphic forms obtained from different solvents at temperatures between -14° and +19° C., the reader is referred to a later publication of von Sydow (156a).

Stenhagen and co-workers reported the synthesis of several long-chain iso- or methyl-branched acids, i.e., long-chain acids containing an isopropyl group, $-\text{CH}(\text{CH}_3)_2$, at the end of the chain opposite the carboxyl group (157). Long-chain keto compounds were prepared by a method involving the mono-alkylation of a long-chain β -keto ester and ketonic cleavage of the alkylation product (158). Reduction of this keto acid gives the normal long-chain acid. Similar alkylation of a long-chain iso- β -keto ester with the appropriate ω -iodo ester yields the isoketo acid, which on reduction by Clemmensen's method, gives the iso acid (157,159). Clemmensen reduction using *n*-propanol and dry hydrogen chloride gave the propyl esters which were converted into the corresponding alcohols by high-pressure hydrogenation over copper chromite. The alcohols were converted into the iodides which were used in a Wurtz reaction to prepare very long chain hydrocarbons (160).

Thermal and x-ray diffraction properties were used to characterize individual compounds. Melting points and x-ray long spacings, by means of which several of these compounds can be identified, are given in Table 56.

Stenhagen and co-workers found no evidence of polymorphism for iso acids having 26 carbon atoms or less. Thus, while stearic acid is known to have three crystalline modifications, isostearic acid appears to have only one stable form (157). The C_{35} -acid, however, has two crystalline modifications. The even-numbered carbon acids form an isomorphous series, but in the odd-numbered series the C_{13} - and C_{15} -acids form a separate group with a structure different from that of the higher members (159). As has been shown, the melting points of the normal long-chain acids show alternation between odd and even members of the series, the even-numbered acids having higher melting points than the odd-numbered acids containing one more carbon atom. The melting points of the iso acids follow a similar pattern and they lie about 1° lower than those of the straight-chain acids with the same number of carbon atoms. The alternation might have been expected to follow the number of carbon atoms in the long chain, in which case the odd-numbered iso acids would show the higher melting points, but this was not found to be the case (157).

X-ray data for 17 normal 3(β)-keto acids with 8 to 24 carbon atoms are given in Table 56. No polymorphism has been observed for the even-numbered acids, and the long spacings of these acids, when plotted against the number of carbon atoms, fall on a straight line, indicating that they form an isomorphous series. The odd-numbered acids also seem to form an isomorphous series, and their long spacings appear to fall on a line lying slightly above that of the even-numbered members. Specimens of the C₁₅-, C₁₉-, and C₂₃-acids crystallized from acetone were found to be mixtures of two different crystalline modifications (163).

The long spacings of the methyl ketones, formed on thermal decomposition of the β -keto acids, are included in Table 56. These ketones crystallize in the orthorhombic system with vertical double molecules. The spacings for both odd- and even-numbered ketones fall on the same straight line and no polymorphism was reported (163).

ω -Trimethyl-substituted acids show a much lower melting point than the normal chain or the ω -dimethyl-substituted isomers (iso acids). ω -Neopentyl-substituted keto acids are abnormal with respect to their melting points, which are lower than those of the corresponding reduced acids, a phenomenon that occurs very rarely in the case of long-chain acids (162).

Normal primary alcohols, as pointed out earlier, crystallize with two molecules arranged end-to-end, and the higher electron density in the middle of the unit cell produced by the presence of the two polar groups gives rise to the characteristic alternation with strong odd and weak even orders. However, Stenhagen and Tägtström-Eketorp (157) have shown that in 16-methylheptadecanol the methyl groups at the end of the chain make the electron density at the end and in the middle of the unit cell nearly the same, with the result that alternation disappears and the intensity distribution among the first eight orders of the long spacing resembles that shown by *n*-hydrocarbons.

Piper *et al.* (45) have shown that the melting points of the odd- and even-numbered, long-chain *n*-alcohols lie on one curve and that this indicates that the chains are vertical (A-form) at the melting point. The odd-numbered alcohols crystallize in the A-form at room temperature, but the even-numbered alcohols crystallize with tilted chains (B-form) and it is assumed that they adopt the A-form near the melting point. Stållberg *et al.* (160) point out that this is certainly not true for higher alcohols with more than 29 carbon atoms. The C₂₉- and C₃₁-alcohols, prepared in the A-form at room temperature, change to a tilted form (B') just before melting. A specimen of the C₃₂-alcohol was found to retain the B-form up to the melting point. It seems likely, therefore,

TABLE 56

Melting Points and X-Ray Long Spacings of Iso-, Keto, and Ketoiso Acids and Derivatives

Compound	Empirical formula	M.p., ° C.	Long spacing, A.	Reference
<i>Iso- or methyl-branched acids</i>				
11-Methyldodecanoic	C ₁₃ H ₂₆ O ₂	40.6–41.3	26.2	159
12-Methyltridecanoic	C ₁₄ H ₂₈ O ₂	53.3–53.6	27.0	159
13-Methyltetradecanoic	C ₁₅ H ₃₀ O ₂	51.7–51.8	29.8	159
14-Methylpentadecanoic	C ₁₆ H ₃₂ O ₂	61.5–61.6	30.4	159
15-Methylhexadecanoic	C ₁₇ H ₃₄ O ₂	59.3–59.8	33.35	159
16-Methylheptadecanoic	C ₁₈ H ₃₆ O ₂	67.8–68.5	33.8	159
17-Methyloctadecanoic	C ₁₉ H ₃₈ O ₂	67.3–67.8 ^a	36.2	159
22-Methyltricosanoic	C ₂₄ H ₄₈ O ₂	83.1–83.5	44.4	159
23-Methyltetracosanoic	C ₂₅ H ₅₀ O ₂	82.4–82.6	47.6	159
24-Methylpentacosanoic	C ₂₆ H ₅₂ O ₂	86.4–86.7	48.4	159
33-Methyltetratriacontanoic	C ₃₅ H ₇₀ O ₂	95.4–95.8	65.4 and 56.0	150
20,20-Dimethylheneicosanoic	C ₂₃ H ₄₆ O ₂	63.3–63.8	40.0	162
<i>Ketoiso acids</i>				
7-Keto-11-methyldodecanoic	C ₁₃ H ₂₄ O ₃	49.1–50.1	26.5	159
11-Keto-13-methyltetradecanoic	C ₁₅ H ₂₈ O ₃	61.6–61.9	29.3	159
12-Keto-14-methylpentadecanoic	C ₁₆ H ₃₀ O ₃	64.6–65.6	30.1	159
11-Keto-15-methylhexadecanoic	C ₁₇ H ₃₂ O ₃	66.8–67.4	33.2	159
12-Keto-22-methyltricosanoic	C ₂₄ H ₄₆ O ₃	87.7–88.1	45.0	159
9-Keto-23-methyltetracosanoic	C ₂₅ H ₄₈ O ₃	88.1–88.4	47.3	159
9-Keto-24-methylpentacosanoic	C ₂₆ H ₅₀ O ₃	92.3–92.5	48.3	159
18-Keto-33-methyltetratriacontanoic	C ₃₅ H ₆₈ O ₃	100.4–100.6	65.9	159
13-Keto-16-methylheptadecanoic	C ₁₈ H ₃₄ O ₃	76.9–77.2	33.7	157
13-Keto-14,14-dimethylpentadecanoic	C ₁₇ H ₃₂ O ₃	40.5–41	31.0	162
19-Keto-20,20-dimethylheneicosanoic	C ₂₃ H ₄₄ O ₃	59.3–59.6	40.0	162
<i>3(β)-Keto and other keto acids</i>				
3-Ketooctanoic	C ₈ H ₁₄ O ₃	68.5–69	20.9	163
3-Ketononanoic	C ₉ H ₁₆ O ₃	68–68.5	23.5	163
3-Ketodecanoic	C ₁₀ H ₁₈ O ₃	79.5–80	24.9	163
3-Ketohendecanoic	C ₁₁ H ₂₀ O ₃	78.5–79	27.6	163
3-Ketododecanoic	C ₁₂ H ₂₂ O ₃	86.5–87	29.4	163
3-Ketotridecanoic	C ₁₃ H ₂₄ O ₃	85.5–86	31.8	163
3-Ketotetradecanoic	C ₁₄ H ₂₆ O ₃	91–91.5	33.8	163
3-Ketopentadecanoic	C ₁₅ H ₂₈ O ₃	90–90.5	35.8 and 42	163
3-Ketohexadecanoic	C ₁₆ H ₃₀ O ₃	95–95.5	37.8	163
3-Ketoheptadecanoic	C ₁₇ H ₃₂ O ₃	95–95.5	40.1	163
3-Ketooctadecanoic	C ₁₈ H ₃₄ O ₃	98–99	42.0	163
3-Ketononadecanoic	C ₁₉ H ₃₆ O ₃	97.5–98	44.3 and 49	163

TABLE 56 (Continued)

Compound	Empirical formula	M.p., ° C.	Long spacing, Å.	Reference
3-Ketoeicosanoic	C ₂₀ H ₃₈ O ₃	100.5–101	46.2	163
3-Ketoheneicosanoic	C ₂₁ H ₄₀ O ₃	100–100.5	48.4	163
3-Ketodocosanoic	C ₂₂ H ₄₂ O ₃	102.5–103	50.3	163
3-Ketotricosanoic	C ₂₃ H ₄₄ O ₃	102.5–103	52.6 and 59	163
3-Ketotetracosanoic	C ₂₄ H ₄₆ O ₃	104.5–105	54.6	
13-Ketotetratriacontanoic	C ₃₄ H ₆₆ O ₃	107.4–107.8	90.7	158
18-Ketooctatetracontanoic	C ₄₈ H ₉₄ O ₃	116.0–116.3	126	160
18-Ketohentriacontanoic	C ₃₁ H ₆₀ O ₃	103.6–104.1	82.4	160
18-Ketopentacontanoic	C ₅₀ H ₉₈ O ₃	116.5–117.3	131	160
<i>Methyl and ethyl ketoesters</i>				
Methyl 3-keto-13-methyltetradecanoate	C ₁₆ H ₃₀ O ₃	37.4–37.8	31.9	159
Methyl 2-keto-octadecane-1,18-dicarboxylate	C ₂₀ H ₃₆ O ₅	71.7–71.9	28.8	159
Methyl 3-ketotetracosanoate	C ₂₅ H ₄₈ O ₃	68.7–68.9	48.7	158
Ethyl 13-keto-16-methylheptadecanoate	C ₂₀ H ₃₈ O ₃	29.8–30.2	20.8	157
<i>Isoalcohols, esters, and other compounds</i>				
13-Methyltetradecanol	C ₁₅ H ₃₂ O	28.8–29.2	27.5	159
14-Methylpentadecanol	C ₁₆ H ₃₄ O	29.4–30.4	31.4	159
15-Methylhexadecanol	C ₁₇ H ₃₆ O	40.7–41.2	30.8	159
16-Methylheptadecanol	C ₁₈ H ₃₈ O	40.1–40.3	34.8	157
<i>n</i> -Nonocosanol	C ₂₉ H ₆₀ O	84.5–84.7	77.8 and 83.0	160
20-Nonatricontanone	C ₃₉ H ₇₈ O	91.2–91.4	51.5	164
<i>n</i> -Propyl- <i>n</i> -hentriacontanoate	C ₃₄ H ₆₈ O ₂	68.6–69.0	40.5 and 45	160
<i>n</i> -Hentriacontanol	C ₃₁ H ₆₄ O	87.0–87.2, 87.4	83.0, 76.0	160
<i>n</i> -Hentetracontanol	C ₄₁ H ₈₄ O	96.3–96.5, 98	108.2, 93.0	160
<i>n</i> -Pentacontanol	C ₅₀ H ₁₀₂ O	104.5–104.7	131	160
<i>n</i> -Propylpentacontanoate	C ₅₃ H ₁₀₆ O ₂	93.4–93.6	70.0 and 61.5	160
<i>n</i> -Propylhentetracontanoate	C ₄₄ H ₈₈ O ₂	84.1–84.3	60.0, 53.0	160
<i>Unsaturated acids and esters</i>				
22-Tricosenoic	C ₂₃ H ₄₄ O ₂	75.1–75.2	49.2	161
Methyl 22-tricosenoate	C ₂₄ H ₄₆ O ₂	49.8–49.9	29.1	161
13-Keto-22-tricosenoic	C ₂₃ H ₄₂ O ₃	86.5–86.7	61.8	161
22-Tricosynoic	C ₂₂ H ₄₂ O ₂	89.9–90.1	53.1	161

TABLE 56 (Continued)

Compound	Empirical formula	M.p., ° C.	Long spacing, Å.	Reference
Methyl 22-tricosynoate	C ₂₄ H ₄₄ O ₂	62.9–63.2	56.5	161
21-Tricosynoic	C ₂₃ H ₄₂ O ₂	84.5–84.7	49.2	161
Methyl 21-tricosynoate	C ₂₄ H ₄₄ O ₂	43.9–44.0	32.7	161
		47.3–47.7	48.8	
<i>Isoacid amides</i>				
11-Methyldodecanamide	C ₁₃ H ₂₇ ON	97.8	25.6	159
12-Methyltridecanamide	C ₁₄ H ₂₉ ON	107.8–107.4	26.7	159
13-Methyltetradecanamide	C ₁₅ H ₃₁ ON	97.0–97.5	29.0	159
14-Methylpentadecanamide	C ₁₆ H ₃₃ ON	101.4–101.7	30.0	159
15-Methylhexadecanamide	C ₁₇ H ₃₅ ON	98.2–98.7	33.6	159
16-Methylheptadecanamide	C ₁₈ H ₃₇ ON	106.4–106.8	33.1 and 34.5	159
17-Methyloctadecanamide	C ₁₉ H ₃₉ ON	100.2–102.3	36.9	159
22-Methyltricosanamide	C ₂₄ H ₄₉ ON	110.5–110.7	43.1	159
23-Methyltetracosanamide	C ₂₅ H ₅₁ ON	108.6–109.1	48.2	159
24-Methylpentacosanamide	C ₂₆ H ₅₃ ON	112.2–112.6	46.3	159
33-Methyltetratriacontanamide	C ₃₅ H ₇₁ ON	116.4–116.7	65.9 and 63.3	159
20,20-Dimethylheneicosanamide	C ₂₃ H ₄₇ ON	98.0–98.3	38.8	162
14,14-Dimethylpentadecanamide	C ₁₇ H ₃₅ ON	104.0–104.5	24.7	162
16-Methylheptadecanamide	C ₁₈ H ₃₇ ON	106.4–106.8	33.1	162

^a Synthesized by J. Cason, *J. Am. Chem. Soc.*, **64**, 1106–1110 (1942).

that the higher alcohols show alternation in the melting points, with the odd-numbered alcohols falling on a curve lying very slightly below that of the even-numbered ones. The entire question of the polymorphism of long-chain alcohols near their melting points needs further study.

Thermal properties and x-ray spacings for the isoacid amides are included in Table 56. The melting-point data for the lower members of the amides, in the range C₁₃ to C₁₈, are very irregular. A regular odd-even alternation of the usual type exists only for the amides having more than 18 carbon atoms. X-ray data afford an explanation for these results. In the range of C₁₃ to C₁₈, only the C₁₆- and C₁₈-amides are isomorphous. For the C₁₄- and C₁₅-amides only one crystalline modification has been found. All the others are dimorphic. Each of these six amides appears to have a different crystal form. From the C₁₆-member upward, the even-numbered amides obtained from solvents form an isomorphous series. The form of the C₁₇-amide, obtained after previous melting, appears to be isomorphous with the single modification found for the C₂₅-amide and

with the form of the C_{35} -amide obtained from solvents. Arosenius *et al.* (159) believe that their results on the amides "would seem to quash the evidence put forward in favour of the spiral-structure hypothesis" (165, 166). The results now obtained do not seem to support the spiral-structure hypothesis and it is possible to explain the x-ray results on the basis of the usual plane zigzag configuration of the hydrocarbon chain.

The contributions to x-ray diffraction and polymorphism of Stenhagen and co-workers have been limited mainly to an investigation of iso acids and their derivatives. No extensive investigation has been made of the polymorphism or of the x-ray diffraction of other branched-chain fatty acids or of their derivatives. Cason, his students, and co-workers (167) have published a series of more than thirty reports on the preparation

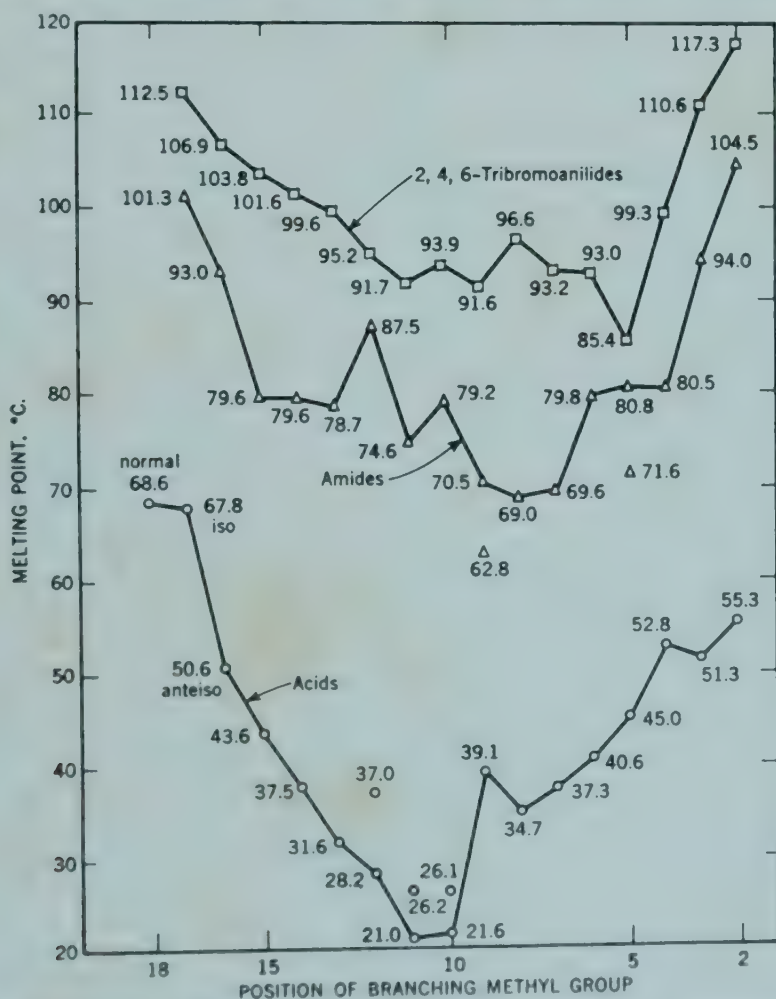


Fig 13 Melting points of methyloctadecanoic acids and their derivatives (168).

and properties of branched-chain fatty acids. They included melting points, but no x-ray diffraction data for these compounds. The melting points for an extended series of branched-chain fatty acids have been collected in Table 5 (Chapter II) and a plot of some of these by Cason (168) are shown in Figure 13.

TABLE 57

Melting Points and X-Ray Long Spacings of Branched-Chain Acids, Amides, and Intermediates

Compound	Formula	M.p., ° C.	Long spacing, Å.
<i>Methyl esters of n-3(β)-keto acids (169)</i>			
Methyl 3-ketononanoate	C ₁₀ H ₁₈ O ₃	-21, ^a -13 ^b	—
Methyl 3-ketodecanoate	C ₁₁ H ₂₀ O ₃	-10.5, ^a -6.5	—
Methyl 3-ketoundecanoate	C ₁₂ H ₂₂ O ₃	-1.1, ^a +4.0 ^b	—
Methyl 3-ketododecanoate	C ₁₃ H ₂₄ O ₃	+11.5, ^a +12.7	—
Methyl 3-ketotridecanoate	C ₁₄ H ₂₆ O ₃	21.1, ^a 22.7 ^b	20.1
Methyl 3-ketotetradecanoate	C ₁₅ H ₂₈ O ₃	28.7	31.1
Methyl 3-ketopentadecanoate	C ₁₆ H ₃₀ O ₃	33.3, 34.0	38.5, 26.5
Methyl 3-ketohexadecanoate	C ₁₇ H ₃₂ O ₃	40.1	34.8
Methyl 3-ketoheptadecanoate	C ₁₈ H ₃₄ O ₃	41.4, 42.7	36.7, 42.7
Methyl 3-ketooctadecanoate	C ₁₉ H ₃₆ O ₃	49.2	38.3
Methyl 3-ketononadecanoate	C ₂₀ H ₃₈ O ₃	50.4	40.2
Methyl 3-ketoeicosanoate	C ₂₁ H ₄₀ O ₃	56.4	41.65
Methyl 3-ketoheneicosanoate	C ₂₂ H ₄₂ O ₃	56.9	43.6
Methyl 3-ketodocosanoate	C ₂₃ H ₄₄ O ₃	62.6	45.3
Methyl 3-ketotricosanoate	C ₂₄ H ₄₆ O ₃	63.2	47.2
Methyl 3-ketotetracosanoate	C ₂₅ H ₄₈ O ₃	68.6	48.8
<i>Iso- and ketoiso acids and amides (170,171)</i>			
13-Keto-14-methylheptadecanoic acid	C ₁₈ H ₃₄ O ₃	45.5-45.9	33.8
14-Methylheptadecanoic acid	C ₁₈ H ₃₆ O ₂	42.7-43.0	33.4
14-Methylheptadecanamide	C ₁₈ H ₃₇ ON	81.5-82.0	34.7
13-Keto-14-methyloctadecanoic acid	C ₁₉ H ₃₆ O ₃	39.2-40.0	35.4
14-Methyloctadecanoic acid	C ₁₉ H ₃₈ O ₂	36.3-36.5	35.4
14-Methyloctadecanamide	C ₁₉ H ₃₉ ON	79.0-79.3	36.8
11-Keto-12-methyltetracosanoic acid	C ₂₅ H ₄₈ O ₃	48.1-48.4	46.9
12-Methyltetracosanoic acid	C ₂₅ H ₅₀ O ₂	43.8-44.6	49.2
12-Methyltetracosanamide	C ₂₅ H ₅₁ ON	86.7-86.9	48.7
13-Keto-15-methylheptadecanoic acid	C ₁₈ H ₃₄ O ₃	54.6-54.8	33.0
15-Methylheptadecanoic acid	C ₁₈ H ₃₆ O ₂	43.5-43.7	29.3
15-Methylheptadecanamide	C ₁₈ H ₃₇ ON	84.5-84.8	27.3

^a Transparent.

^b Opaque.

TABLE 58
Melting Points and X-ray Spacings of Keto-octadecanoic Acids and Methyl Esters (172)

Position of sub- stituent	Crystal spacing, A.			Crystal spacing, A.		
	M.p., ° C.	Long	Short	M.p., ° C.	Long	Short
		<i>Acids</i>			<i>Esters</i>	
2	74.3-74.6	49.7	4.15, 3.58	54.0-54.1	38.7	3.66, 4.05, 4.56, 4.98
3	99 (dec.)	42.0	4.45, 4.25, 3.87 3.65	49.2	38.3	4.63, 4.40, 3.88 3.69, 3.55, 3.39
4	96.3-96.5	49.7	4.68, 4.48, 4.01 3.63	47.9-48.0	45.6	4.27, 4.04, 3.90 3.72, 3.56
5	94.2-94.3	38.4	—	54.3-54.5	49.6	4.46, 4.28, 4.05 3.78
6	87.1-87.3	49.7	—	46.3-46.8	47.6	3.73, 4.03, 4.27, 4.44
7	91.4-91.6	49.7	4.10, 3.80, 2.99	48.7-48.8	47.6	3.73, 4.03, 4.27, 4.44
8	86.6-86.8	49.7	—	46.4-46.9	47.6	3.73, 4.03, 4.27, 4.44
9	83.6-83.8	49.7	4.10, 3.80, 2.99	47.5-48.0	47.6	3.73, 4.03, 4.27, 4.44
10	81.7-81.9	49.7	4.10, 3.80, 2.99	45.8-46.1	47.6	3.73, 4.03, 4.27, 4.44
11	82.4-82.6	49.7	4.10, 3.80, 2.99	46.7-46.9	47.6	3.73, 4.03, 4.27, 4.44
12	81.7-81.9	49.7	4.10, 3.80, 2.99	45.4-45.7	47.6	3.73, 4.03, 4.27, 4.44
13	81.5-81.9	49.7	4.10, 3.80, 2.99	47.3-47.7	47.6	3.73, 4.03, 4.27, 4.44
14	82.1-82.3	49.7	4.10, 3.80, 2.99	48.9-49.0	53.5	4.11, 3.76, 2.99
15	81.7-81.9	49.7	4.10, 3.80, 2.99	53.5-53.7	47.6 and 53	4.11, 3.76, 2.99
16	83.0-83.2	49.7	4.10, 3.80, 2.99	54.3-54.5	53.5	
17	93.1-93.5	49.7	4.50, 3.76, 3.64	56.1-56.5	47.6 and 53	
	87.4-87.7	49.7	4.30, 3.82			

TABLE 58a
Melting Points and X-ray Spacings of Monohydroxyoctadecanoic Acids and Methyl Esters (172)

Position of sub- stituent	M.p., ° C.	Crystal spacing, Å.		M.p., ° C.	Crystal spacing, Å.	
		Long	Short		Long	Short
2	90.9-91.1	41.9 and 49	3.84, 4.33, 4.78	65.7-65.9	26.4	4.18, 3.64
3	89.4-89.6	46.5, 44.6 and 36.0	4.11, 3.89	51.1-51.4	47.5	4.34, 4.11, 3.89
4	87.0-87.4	44.1	4.36, 4.08, 3.90	56.1-56.4	47.5	
				57.2-57.4	47.5 and 52	4.34, 4.11, 3.89
				58.6-59.3		
5	81.9-82.1	44.1	4.36, 4.08, 3.90	51.7-52.1	47.5	4.34, 4.11, 3.89
6	82.0-82.4	44.4	4.36, 4.08, 3.90	58.2-58.5	47.5	4.34, 4.11, 3.89
7	77.6-77.8	44.4	4.36, 4.08, 3.90	50.7-51.0	47.5	4.34, 4.11, 3.89
8	81.5-81.7	44.4	4.36, 4.08, 3.90	55.3-55.6	47.5	4.34, 4.11, 3.89
				45		
9	75.4-75.9	44.4 and 47.5	4.36, 4.08, 3.90	50.3-50.6	47.5 and 52	4.34, 4.11, 3.89
				45.0-45.3		

10	79.2-79.5	44.3	4.36, 4.08, 3.90	45; 54.1-2 51.5-52	47.5 and 52	4.34, 4.11, 3.89
11	77.2-77.5	44.3 and 47.5	4.36, 4.08, 3.90	49.6-49.8 48	47.5 and 52	4.34, 4.11, 3.89
12	76.6-76.9 78.5-79.9	44.3	4.36, 4.08, 3.90	53.4-53.6 52.3-52.7	47.5 and 52	4.34, 4.11, 3.89
13	77.2-77.5	47.5 and 44.3	4.18, 3.85	53.3-53.5 52.0-52.4	47.5 and 52	4.34, 4.11, 3.89
14	76.6-76.8 79.6-79.9	44.3 and 42.4	—	54.5-54.8 54	47.5 and 52	4.34, 4.11, 3.89
15	75.3-75.5	47.5 and 44.3 42.2	4.18, 3.85	58.7-58.9 51	47.5	4.34, 4.11, 3.89
16	78.4-78.6	44.3	4.36, 4.08, 3.90	61.2-61.5 56	40.6 and 47.8	—
17	76.4-76.6 81.0-81.4	40.2	4.36, 4.11, 3.93, 3.63	64.1-64.8 52 -52.5	47.5	4.64, 4.29, 4.07, 3.72
18	99.3-99.5 87.0-88.0	46.8	4.61, 3.78, 3.46	62.4-62.6 (38.5 form)	38.5 and 48	—

Ställberg-Stenhagen (169) described the synthesis of the methyl esters of normal 3(β)-keto acids and the preparation of branched-chain acids using these compounds as intermediates (170,171). The methyl esters of the normal 3-keto acids, keto methyl-branched acids and their methyl-branched amides have been characterized by melting points and x-ray long spacings. These data, which are given in Table 57, include those for the few x-ray spacings of branched-chain fatty acids, other than iso acids, which have thus far become available. The identification of branched-chain hexanoic acids by x-ray diffraction patterns of their silver salts has been proposed by Guertin *et al.* (168a).

Bergstrom *et al.* (172) reported data for the thermal and x-ray properties of the homologous series of monoketo- and monohydroxyoctadecanoic acids and their methyl esters. They found polymorphism of the keto compounds to be relatively uncomplicated and hence more applicable for identification purposes, and they recommend therefore that hydroxy acids be converted to the corresponding keto acids for purposes of identification. A combination of thermal and x-ray diffraction data (Tables 58 and 58a) should permit the identification of any keto or hydroxyoctadecanoic acid, using only milligram quantities of material. Identification can be made readily and accurately from the data for either the keto or the hydroxy acids, if the unknown position of the substituent is near either end of the chain. If near the center of the chain, the uncertainty of the identification can be reduced by conversion of the keto acids to the methyl esters. These compounds with the substituent in the 6th to the 13th position do not exhibit polymorphism. Final identification can be made, as shown by Bergstrom *et al.* (172), by use of Shearer's (40) intensity distribution of the successive orders of reflection previously described.

Cavanni and Ställberg-Stenhagen (173) and Ställberg-Stenhagen (174) have contributed a series of a dozen or more reports from the University of Uppsala describing the preparation and properties, including x-ray diffraction and thermal data, for a number of optically active, long-chain, aliphatic compounds, mostly acids, esters, and salts. Many other examples of the use of x-ray diffraction and thermal data for the analysis or characterization of aliphatic acids and their derivatives may be cited, a few of which are mentioned below.

Velick (175) resorted to the use of x-ray diffraction to prove the homology of a series of iso acids obtained from wool fat, and Schuette and Baldinus (176) applied this technique to characterize the *n*-paraffins isolated from candelilla wax. Murry and Schoenfeld used x-ray data in

investigations of the normal alcohols of wool wax (177) and of the diols and hydroxy acids (179) of carnauba wax. Kreger and Schamhart (180) investigated the x-ray long spacings of synthetic esters of the saturated straight-chain C_{16} to C_{20} fatty acids and C_{12} to C_{22} primary alcohols, thus obtaining their own standards for comparison with the data obtained with the esters of natural cuticle wax. From their x-ray data and the application of Shearer's method of intensity distribution for locating the position of the carbonyl group in ketones and esters, new information concerning the constitution of the cuticle waxes was obtained solely from x-ray patterns.

Huber (181) and Huber *et al.* (182) reported data for the x-ray diffraction and polymorphism of mono- α -amino-acyl and mono- α -dipeptide triglycerides. Chibnall *et al.* (183) described the use of x-ray diffraction data for identifying long-chain paraffin constituents of rose-petal wax.

Hansen *et al.* (184–186) published reports which illustrate very well the manner in which previously compiled x-ray diffraction data may be applied to solve problems of constitution or identification of fatty acid materials. They were able to identify *n*-heptadecanoic and *n*-pentadecanoic acids from hydrogenated mutton fat by direct comparison of their x-ray diffraction data with those of Francis and Piper (56), Slagle and Ott (57), and Francis *et al.* (58). X-ray patterns were also used to show that certain fractions were not 15-methylhexadecanoic or 14-methylhexadecanoic acids by direct comparison with the x-ray diffraction data of Arosenius *et al.* (159). In a similar manner, 12-methyltridecanoic acid was identified as a constituent of butter fat (187) by direct comparison with the data of Arosenius *et al.* (159) and that it was not *n*-tetradecanoic acid by comparison with the data of Francis and Piper (56).

From the foregoing review it is apparent that x-ray diffraction data are being increasingly used for the identification and characterization of many and varied types of fatty materials.

8. Complete Crystallographic Data

The data reviewed and discussed in this chapter were obtained by the powder-pattern method of x-ray diffraction (20,21). More complete crystallographic data can be obtained from single crystal measurements. However, the methods involved in making such measurements are considerably more difficult than those involved in powder diffraction, and it

TABLE 59
Crystallographic Data from Single-Crystal Measurements of Aliphatic Acids and Derivatives

Compound	Formula	Axial dimensions, A.			Axial angle			No. Mols. ^a	Density (calc.) g./l.	Ref.
		a	b	c	α	β	γ			
<i>Monocarboxylic acids</i>										
Hendecanoic, C'-form	C ₁₁ H ₂₂ O ₂	9.62	4.92	34.18	—	131°17'	—	4	—	188
Lauric, A-form	C ₁₂ H ₂₄ O ₂	5.41	26.27	35.42	69°36'	113°9'	121°21'	12	1.027	189
Lauric, C-form	C ₁₂ H ₂₄ O ₂	9.52	4.96	35.39	—	129°13'	—	4	1.034	190
Lauric, C-form	C ₁₂ H ₂₄ O ₂	9.63	4.97	35.58	—	129°35'	—	—	—	191
Lauric, γ -form	C ₁₂ H ₂₄ O ₂	22.1	5.24	32.0	90°	99°58'	90°	12	1.09	192
Myristic, C-form	C ₁₄ H ₂₈ O ₂	9.51	4.97	40.71	—	129°7'	—	—	—	191
Myristic γ -form	C ₁₄ H ₂₈ O ₂	22.2	5.14	37.2	90°	100°50'	90°	12	1.09	192
Pentadecanoic, A'-form	C ₁₅ H ₃₀ O ₂	4.25	5.01	42.76	89°50'	111°5'	112°10'	2	1.034	193
Pentadecanoic, B'-form	C ₁₅ H ₃₀ O ₂	5.54	8.06	42.58	114°18'	114°13'	80°37'	4	1.018	194
Isopalmitic	C ₁₆ H ₃₂ O ₂	5.09	5.68	48.1	140°0'	111°1'	72°7'	2	1.020	195
Stearic	C ₁₈ H ₃₆ O ₂	5.55	7.38	48.84	—	63°38'	—	4	—	196
Stearic, B-form	C ₁₈ H ₃₆ O ₂	5.59	7.40	49.38	—	117°22'	—	4	—	197
Stearic, C-form	C ₁₈ H ₃₆ O ₂	9.36	4.96	50.76	—	128°14'	—	—	—	191
<i>trans</i> -9-Linoleic	C ₁₈ H ₃₂ O ₂	95.69	4.95	7.31	—	90°6'	—	8	1.07	198
14-Ethylhexadecanoic	C ₁₈ H ₃₆ O ₂	5.58	6.79	27.96	93°15'	111°30'	100°14'	2	0.982	199
16-Methyloctadecanoic	C ₂₀ H ₄₀ O ₂	5.43	6.91	28.00	91°16'	94°16'	104°56'	2	0.979	199
17-Methyloctadecanoic	C ₂₀ H ₄₀ O ₂	5.64	9.66	37.10	90°24'	91°38'	102°33'	4	1.004	199
Stearolic	C ₁₈ H ₃₂ O ₂	9.55	4.69	49.15	—	53°4'	—	4	—	196
Behenolic	C ₂₂ H ₄₀ O ₂	9.55	4.69	59.10	—	53°30'	—	4	—	196
Behenic, C-form	C ₂₂ H ₄₄ O ₂	9.29	4.95	60.87	—	127°37'	—	—	—	191
Cerotic, C-form	C ₂₆ H ₅₂ O ₂	9.25	4.95	71.18	—	127°19'	—	—	—	191

<i>Dicarboxylic acids</i>										
Adipic	C ₆ H ₁₀ O ₄	10.27	5.16	10.02	—	137°5'	—	2	1.340	200
Pimelic	C ₇ H ₁₂ O ₄	9.93	4.82	22.12	—	130°40'	—	4	1.313	200
Suberic	C ₈ H ₁₄ O ₄	10.12	5.06	12.58	—	135°0'	—	2	1.270	200
Azelaic, α-form	C ₉ H ₁₆ O ₄	9.72	4.83	27.14	—	129°30'	—	4	—	201
Azelaic, β-form	C ₉ H ₁₆ O ₄	5.61	9.58	27.20	—	136°30'	—	4	—	201
Sebacic	C ₁₀ H ₁₈ O ₄	10.05	4.96	15.02	—	133°50'	—	2	1.240	200
Brassylic	C ₁₃ H ₂₄ O ₄	9.63	4.82	37.95	—	128°20'	—	4	1.173	200
Hexadecanedicarboxylic	C ₁₈ H ₃₄ O ₄	9.76	4.92	25.10	—	131°10'	—	2	1.138	200
<i>Potassium salts</i>										
Butyrate, A-form	C ₄ H ₇ O ₂ K	8.10	5.68	14.40	90°	92°	90°	4	1.256	204
Caproate, A-form	C ₆ H ₁₁ O ₂ K	7.98	5.73	18.90	90°	91.9°	90°	4	1.177	204
Caproate, A-form	C ₆ H ₁₁ O ₂ K	7.97	5.73	18.90	—	92°	—	4	—	205
Caprylate, A-form	C ₈ H ₁₅ O ₂ K	7.90	5.67	22.96	90°	92.1°	90°	4	1.170	204
Caprate, A-form	C ₁₀ H ₁₉ O ₂ K	8.06	5.67	27.52	90°	93.5°	90°	4	1.105	204
Caprate, A-form	C ₁₀ H ₁₉ O ₂ K	8.12	5.65	28.91	—	108°2'	—	4	1.108	206
Laurate, A-form	C ₁₂ H ₂₃ O ₂ K	7.95	5.66	31.72	90°	95.7°	90°	4	1.106	204
Laurate, B-form	C ₁₂ H ₂₃ O ₂ K	4.13	5.59	29.98	97.4°	92.0°	94°	2	1.149	204
Myristate, B-form	C ₁₄ H ₂₇ O ₂ K	4.14	5.60	34.00	91.6°	91.5°	93°	2	1.118	204
Palmitate, B-form	C ₁₆ H ₃₁ O ₂ K	4.16	5.60	38.19	92.7°	91.3°	93°	2	1.096	204
Stearate, B-form	C ₁₈ H ₃₅ O ₂ K	4.15	5.56	42.03	91.5°	91.6°	94°	2	1.102	204
Caprylate, C-form	C ₈ H ₁₅ O ₂ K	8.07	5.72	23.76	90°	91.7°	90°	4	1.097	204
Caprate, C-form	C ₁₀ H ₁₉ O ₂ K	8.10	5.67	28.01	90°	91.8°	90°	4	1.079	204
Laurate, C-form	C ₁₂ H ₂₃ O ₂ K	8.06	5.66	32.30	90°	94.2°	90°	4	1.071	204
Myristate, C-form	C ₁₄ H ₂₇ O ₂ K	8.06	5.68	36.87	90°	92.1°	90°	4	1.042	204
Palmitate, C-form	C ₁₆ H ₃₁ O ₂ K	8.03	5.70	40.95	90°	90.1°	90°	4	1.038	204
Stearate, C-form	C ₁₈ H ₃₅ O ₂ K	8.05	5.66	45.37	90°	93.2°	90°	4	1.031	204

(continued)

TABLE 59 (Continued)

Compound	Formula	Axial dimensions, A.			Axial angle			No. Mols. ^a	Density (calc.) g./l.	Ref.
		a	b	c	α	β	γ			
<i>Silver salts</i>										
Caproate	C ₆ H ₁₁ O ₂ Ag	4.59	4.02	20.41	80°16'	81°11'	80°4'	2 ^b	2.062	207
Caprylate	C ₈ H ₁₅ O ₂ Ag	4.62	4.08	25.24	78°42'	84°11'	79°38'	2	1.843	207
Caprate	C ₁₀ H ₁₉ O ₂ Ag	4.65	4.07	30.31	77°53'	85°22'	78°57'	2	1.695	207
Laurate	C ₁₂ H ₂₃ O ₂ Ag	4.65	4.10	35.33	77°1'	86°35'	77°53'	2	1.597	207
Myristate	C ₁₄ H ₂₇ O ₂ Ag	4.66	4.10	40.30	76°32'	87°39'	78°23'	2	1.521	207
Palmitate	C ₁₆ H ₃₁ O ₂ Ag	4.68	4.13	45.32	76°23'	88°58'	77°3'	2	1.463	207
Stearate	C ₁₈ H ₃₅ O ₂ Ag	4.69	4.12	50.35	76°1'	89°28'	76°1'	2	1.423	207
<i>Hydrazides</i>										
Hexanoic acid	C ₅ H ₁₁ CONHNH ₂	7.49	4.88	43.47	—	91°16'	—	8	1.09	208
Heptanoic acid	C ₆ H ₁₃ CONHNH ₂	7.44	4.88	48.60	—	96°14'	—	8	1.09	208
Octanoic acid	C ₇ H ₁₅ CONHNH ₂	7.46	4.87	53.47	—	91°20'	—	8	1.08	208
Nonanoic acid	C ₈ H ₁₇ CONHNH ₂	7.44	4.87	58.73	—	95°4'	—	8	1.08	208
<i>Other derivatives</i>										
Bromostearic acid	C ₁₈ H ₃₅ O ₂ Br	11.04	4.91	52.84	—	43°17'	—	4	—	196
Trilaurin, β -form	C ₃₉ H ₇₄ O ₆	12.31	5.40	31.77	94°16'	96°52'	99°12'	2	1.027	209
Dodecyl ammonium chloride	C ₁₂ H ₂₅ NH ₃ Cl	5.68	7.16	17.86	—	91°2'	—	2	1.034	202
Dodecyl ammonium bromide	C ₁₂ H ₂₅ NH ₃ Br	6.06	7.02	35.8	—	91°6'	—	4	1.162	202
Strontium laurate	(C ₁₂ H ₂₃ O ₂) ₂ Sr	7.80	70.86	4.75	—	102°36'	—	4	1.25	203

^a Number of molecules per unit cell.^b See Figure 4 and accompanying text for significance of these following measurements.

is not easy and often impossible to obtain crystals satisfactory for such measurements. Considerable time and effort are required to compute unit-cell dimensions from such data. For these reasons, comparisons of data obtained by the powder-pattern technique for a given material with similar data previously derived from materials of known configuration and polymorphic form have proven more valuable for analytical purposes. Complete crystallographic data have been obtained for only a relatively few fatty acids and derivatives. Some of these have been compiled in Table 59.

Booth (210) proposed what has been called a method of steepest descents to avoid some of the complications of Fourier synthesis in calculating crystallographic data. Vand and co-workers (211–215) used modifications of this method to study the crystal structure of potassium caproate and lauric acid. Lomer (216) also described an application of Booth's method to the determination of the structure of potassium caproate.

Vand (217,218) described three indexing methods for obtaining complete crystallographic data from powder photographs of long-spacing compounds. As an example of the third method, a graphic procedure, the unit cell of potassium caproate was derived from powder-pattern data. Machines for calculating the structural factors by these methods have been described (219–221).

Vand has also described a direct statistical approach to the determination of crystal structure (222,223) and von Sydow and Vand have reviewed the crystal structures of some phases of normal, long-chain, carboxylic acids (224), as well as the classification of phases in crystals of long-chain compounds and some mechanisms of their phase transition (225).

As stated in the introduction, the scope of this chapter is limited to a discussion of the use of x-ray diffraction to investigate crystal properties of fatty acids and their derivatives. X-rays are a portion of the electromagnetic spectrum and as such are properly a tool of spectroscopy. Spectroscopic uses of x-radiation are not limited to diffraction. Applications of x-ray emission (or fluorescence) and x-ray absorption pertain to the spectral properties rather than to crystal properties of a substance. These subjects are discussed in Chapter V.

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CHAPTER V

SPECTRAL PROPERTIES

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1. Introduction

The complete electromagnetic spectrum comprises radiations arranged in order from the shortest to the longest wavelengths, a range from trillions of a millimeter to thousands of kilometers. Spectroscopy, including x-ray and microwave spectroscopy, is generally limited to the region between about 10^{-2} m μ in the extremely hard x-ray region at the edge of the gamma-ray region, to about 10 cm., the limit of microwaves at the edge of long-wave radio waves. As shown by the diagram in Figure 14, the entire spectrum is conveniently divided into five sections

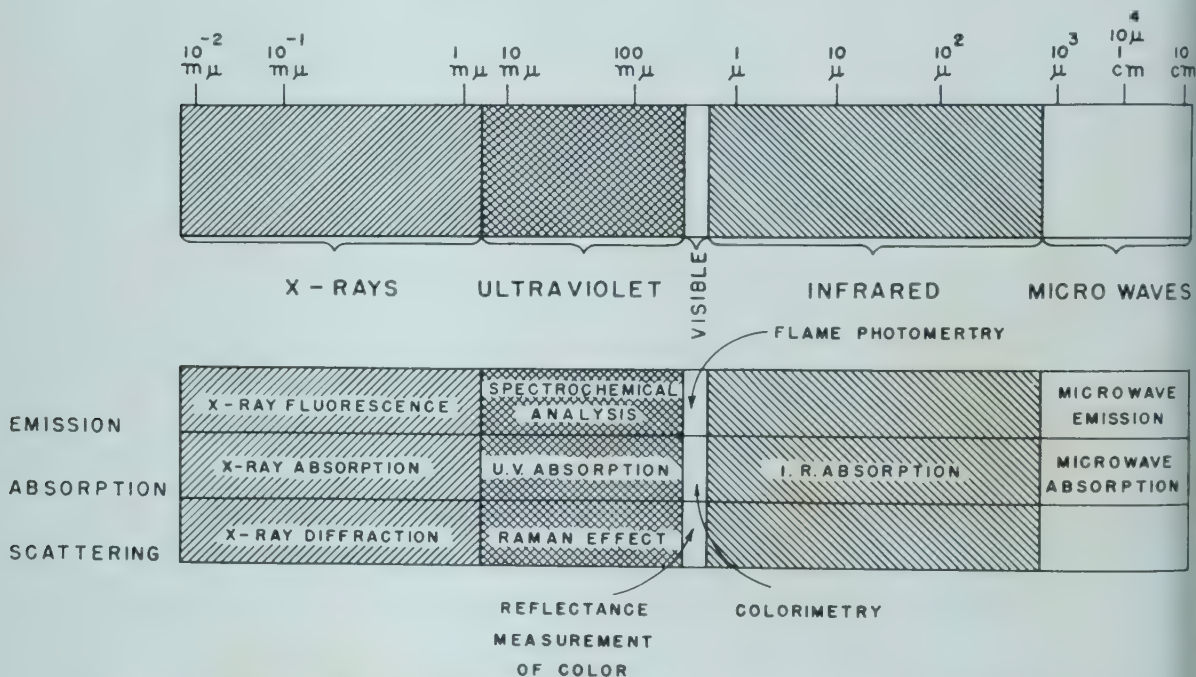


Fig. 14. Divisions of the electromagnetic spectrum applicable to chemical spectroscopy (29).

based roughly on the physical properties of the radiations and the types of detectors required to measure them.

The most obvious division of the electromagnetic spectrum is the visible region bounded by the limits of the human eye as a detector, approximately 400 to 800 m μ . Toward the shorter wavelengths beyond the violet lies the ultraviolet region extending to approximately 2 m μ , and toward still shorter wavelengths lies the x-ray region. Above, or toward longer wavelengths beyond the visible red, lies the infrared region extending to about 1000 μ where it is replaced by the microwave region.

The limits of each division of the electromagnetic spectrum cannot be specified exactly as there is considerable overlapping. An overtone band of the infrared spectrum may involve an energy change sufficiently large to place it within the limits of visible spectrum as defined above. An x-ray transition may occur between two levels sufficiently close together to place the resulting line within what is usually considered the ultraviolet region. The relation between the observed frequency (or wavelength) of any spectral line or band and the energy change involved in the transition which produced it is given by the quantum equation:

$$\Delta E = h\bar{\nu} = hc/\lambda$$

where E is the energy, $\bar{\nu}$ the frequency, h Planck's universal constant, c the speed of light, and λ the wavelength.

X-ray transitions involve energy changes from some hundred volts to more than a hundred thousand volts, while gamma rays involve energy changes of several million volts. Ultraviolet and visible radiation correspond to just a few volts or of the order of 100 kilocalories per mole. Infrared radiations average only about 1 kilocalorie per mole, and microwaves as little as 0.01 kilocalorie per mole. From the quantum equation it can readily be seen that these energies correspond to wavelengths of the order of 300 m μ for the ultraviolet, 30 μ for the infrared, and 3 cm. for the microwave regions, as shown in the diagram in Figure 14.

While the energy change of a transition roughly defines its spectral type, neither energy nor its related frequency or wavelength is the decisive factor. Spectral type is determined by the origin of the transition which gives rise to the observed band or line. Thus, x-ray spectra involve transitions between electronic levels within the kernel of the atom and these levels are generally far apart, i.e., ΔE is large. The ultraviolet region comprises electronic transitions between levels outside of the kernels, i.e., transitions of valence electrons. The visible spectrum is merely an extension of this electronic spectrum where the energy changes are exactly right to produce waves detectable by the human eye. Infrared spectra arise from transitions between vibrational levels within a single electronic level and involve, therefore, considerably smaller energy changes. Finally, microwaves arise from transitions between two rotational levels within a single vibrational level and involve only very small changes in energy.

Radiations in these five divisions of the electromagnetic spectrum may be used in chemical spectroscopy in three ways. The radiation emitted, absorbed, or scattered (or diffracted or reflected) may be employed for analytical purposes. There are, thus, fifteen major divisions of chemical

spectroscopy, as shown in Figure 14. All of these fifteen divisions have been applied to chemical analyses, but not all have found use in the analysis of fatty acids. The regions which have been most useful, or appear to be of greatest potential value, in the applications of spectroscopy to fatty acids are indicated by name in Figure 14.

Spectra may be atomic, involving transitions of excited atoms, or molecular, involving transitions of excited molecules. Atomic spectra consist of single lines, representing changes in energy within the atom from one energy level to another. Molecular spectra are somewhat more complex. The total energy of a molecule is the sum of four types:

$$E = E_{\text{translational}} + E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

Translational energy has no significant effect on spectra and is not considered here. Electronic energy is considerably greater than vibrational energy and rotational energy is considerably less. Within certain restrictions of Pauli's exclusion principle and of the selection rules, the molecule will, in going from one electronic level to another, undergo simultaneously changes in vibrational energy and in rotational energy. As a result, a series of several lines which are very close together in the frequency or wavelength scale occurs. When measured with the dispersion of most instruments used in chemical spectroscopy, these lines are not resolved from one another and emission or absorption is measured over a portion of the electromagnetic spectrum. Such a region is called a band. Molecular spectra result in band spectra, while atomic spectra are line spectra. Thus, the scale (Fig. 14) can be doubled, each division can be used with both atomic and molecular spectra, resulting in a total of 30 different classifications of spectra useful for analytical purposes. In the application of spectroscopy to fatty acid chemistry, it will be made clear in the discussion of each topic whether atomic or molecular spectra are involved.

Applications of spectroscopy depend principally on the fact that a considerable body of spectroscopic data for well-defined substances already exists. Qualitative analysis consists of comparing in some fashion the spectral properties of an unknown with those of identified atoms or molecules. Similarly, quantitative analysis is based on comparisons with carefully measured intensities of "standards" of high purity. Another application depends upon the fact that a study of the spectral properties of compounds of known configuration makes possible the establishment of certain relations between observed spectra and vibrating structures, so that by analogy it is possible to classify fatty acids and their derivatives even though their structures may not be known.

The following discussion is intended to indicate the value of spectroscopy as a tool for investigating fatty acids and fatty acid derivatives and the general types of information which may be derived from the application of spectroscopy to these substances. Lack of space precludes detailed descriptions of the apparatus and details of the methods for measuring the frequency (or wavelength) or the intensity of the various types of spectra which are discussed here, but a number of excellent monographs and articles are available which treat in detail of the theory of spectroscopy, laboratory equipment, and methods of obtaining and measuring various types of spectra (1-12). Manufacturers of spectrographs and spectrophotometers have also made available excellent descriptions of their instruments and brochures on their care and operation in various applications.

Two of the most commonly used units to designate the regions of the spectrum, wavelength (λ) in angstroms (A.), and wavenumber (ν) in reciprocal centimeters, (cm.^{-1}), are shown in the diagram in Figure 14. Frequency ($\bar{\nu}$) is now somewhat less often used. The three terms are intraconvertible and bear the following relations to one another:

$$1/\text{wavelength} = \text{wavenumber} = \text{frequency}/\text{speed of light}$$

or;

$$\text{speed of light}/\text{wavelength} = \text{frequency} = \text{speed of light} \times \text{wavenumber.}$$

It follows that:

$$\begin{aligned} 1/\text{wavelength (in A.)} \times 10^8 &= 1/\text{wavelength (in m}\mu\text{)} \times 10^7 \\ &= \text{wavenumber (in cm.}^{-1}\text{)} \end{aligned}$$

and,

$$10^8/\text{wavenumber (in cm.}^{-1}\text{)} = \text{wavelength (in A.)}$$

and,

$$\begin{aligned} \text{wavenumber (in cm.}^{-1}\text{)} \times 3 \times 10^{-2} &= 3 \times 10^6/\text{wavelength (in A.)} \\ &= 3 \times 10^5/\text{wavelength (in m}\mu\text{)} = \text{frequency (in } f\text{)} \end{aligned}$$

and,

$$3 \times 10^6/\text{frequency (in } f\text{)} = \text{wavelength (in A.)}$$

All spectroscopic terms, units and symbols used in this chapter are those recommended by the Joint Committee on Nomenclature (13). The terms and units most commonly referred to and the symbols used to indicate them include:

Absorbance (A):	The logarithm to the base 10 of the reciprocal of the transmittance. $A = \log_{10} (1/T)$.
Absorption band:	A region of the absorption spectrum in which the absorptivity passes through a maximum or inflection.
Absorptivity (a):	The ratio of the absorbance to the product of concentration and length of optical path. It is the absorbance per unit concentration and thickness—i.e., the specific absorbance $a = A/bc$.
Angstrom (A.):	A unit of length equal to $1/6438.4696$ of the wavelength of the red line of cadmium. This is almost, but not exactly, 10^{-8} cm. or 10^{-10} meter; the difference is not significant in applied spectroscopy.
Frequency ($\bar{\nu}$):	Number of cycles per unit time.
Fresnel (f):	A unit of frequency equal to 10^{12} cycles per second.
Micron (μ):	A unit of length equal to 10^{-6} meter.
Millimicron ($m\mu$):	A unit of length equal to one-thousandth of a micron. It is almost, but not exactly, equal to 10 angstroms.
Radiant power (P):	The rate at which energy is transported in a beam of radiant energy.
Transmittance (T):	The ratio of the radiant power transmitted by a sample (P) to the radiant power incident on the sample (P_0), both measured at the same spectral position and with the same slit width. The beam is understood to be parallel radiation and incident at right angles to plane parallel surfaces of the sample.
Wavelength (λ):	The distance measured along the line of propagation between two points which are in phase on adjacent waves.
Wavenumber (ν):	The number of waves per unit length.

2. X-Ray Spectra

(a) Diffraction

As shown in Figure 14, the wavelength of x-rays lies between 10^{-2} and $1\text{ m}\mu$ or 10^{-7} to 10^{-9} cm. Von Laue calculated from the known number of molecules per unit volume that the average distance between the atoms in solids was between 10^{-7} and 10^{-8} cm. It therefore occurred to him that a crystal may act toward x-rays in much the same manner as a diffraction grating acts toward ordinary light. His experiments confirmed the fact that natural crystals will act as gratings for the diffraction of x-rays. X-ray diffraction has consequently been used to study crystal structure and related phenomena, as discussed in Chapter IV. It should be noted, however, that x-rays are an integral part of the electromagnetic spectrum and that diffraction of radiation in this region falls naturally into one of the main branches of the electromagnetic spectrum as its radiations are used in chemical spectroscopy (see Fig. 14). Besides its very considerable use in the study of crystal structure, x-ray diffraction is also employed for qualitative and quantitative analysis. Its use for the latter purposes was mentioned at the conclusion of Chapter IV.

(b) Absorption

The ability of x-rays to penetrate matter is one of their most striking properties. However, x-rays are absorbed to some extent in passing through matter and x-ray absorption follows the same laws as ordinary light traversing an imperfectly transparent medium (see the Bouguer-Beer law under discussion of ultraviolet absorption). There is, however, one very remarkable difference in the absorption of x-rays and ordinary light. X-ray absorption is an atomic process and absorption by a given element is independent of the chemical combination in which the particular element occurs. The remarkable property of x-ray absorption is that, if the absorptivity of a given mass of matter is considered rather than absorption through a given thickness, i.e., mass absorptivity rather than linear absorptivity, it is found that the mass absorptivity is independent of the state of matter. This may be illustrated by examples from Klug (3). Diamonds are very transparent to light, whereas carbon in the form of graphite is a strong absorber; both, however, have the same mass absorptivity for x-rays. Liquid and solid mercury are opaque to light, but mercury vapor is almost perfectly transparent; all three forms, of course, have the same mass absorptivity to x-rays.

If, with polychromatic x-radiation, the mass absorptivity is plotted against the wavelength, a curve similar to that shown in Figure 15 is obtained. Such a curve is strictly comparable to a plot of absorptivity against wavelength in the region of ultraviolet or visible absorption. The

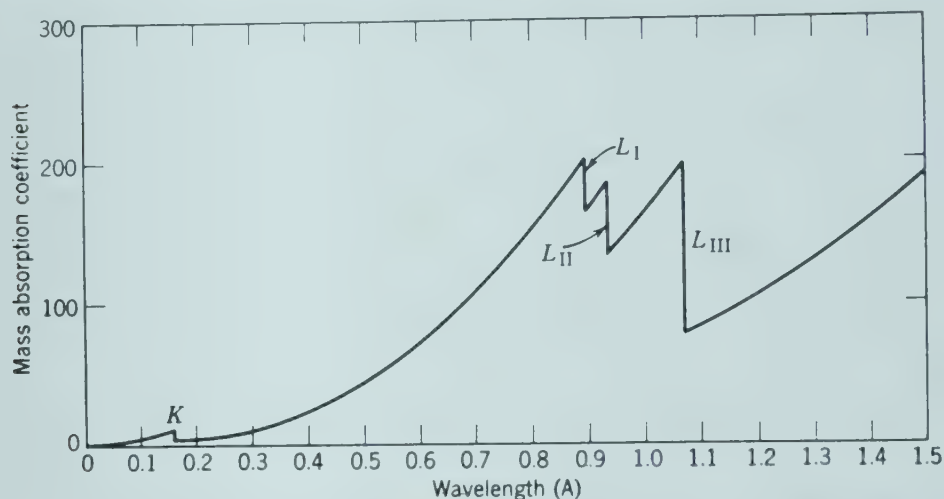


Fig. 15. X-ray absorption spectrum (3). (Reprinted from H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures*, John Wiley, 1954, p. 93.)

mass absorptivity decreases smoothly as the wavelength decreases except for a series of sharp breaks where steep increases are observed. These breaks in the curve are called absorption edges and mark the point on the wavelength scale where the x-rays possess sufficient energy to eject an electron from one of the shells. Thus, in Figure 15, at 0.16 Å., and all wavelengths shorter than this value, the polychromatic beam possesses sufficient energy to eject an electron from the K level. At longer wavelengths, i.e., lower energies, the polychromatic x-ray beam possesses energy sufficient to eject electrons from the three discrete energy levels of the L shell, causing the three discontinuities between 0.0 and 1.1 Å.

The position of the discontinuities identifies the element causing the absorption of x-rays and the magnitude of the break, on the mass absorptivity ordinate, is a measure of its concentration. Thus, a qualitative and quantitative method of analysis is provided. Applications of x-ray absorptiometry have been very few until recently because instruments designed to permit such determinations have not been commercially available. However, during the past few years x-ray photometers have been made available and x-ray absorptiometry is being applied to an increasing number of analyses. While no actual applications to the

analysis of fatty acids have been noted, the increasing use of the technique as in the determination of tetraethyl lead in gasoline (14), sulfur and halogens in hydrocarbon mixtures (15), and of additives in lubricating oils (16) would imply its possible application to fatty acid products.

(c) Fluorescence

When x-rays traverse matter, a part of their energy is spent in ejecting β -rays or electrons from some of the atoms. The remainder of the atom is in an ionized condition and, as it regains its normal state, energy is liberated which reappears as the fluorescent x-rays. When an electron is ejected from the K shell, an electron from the next shell, the L shell, drops into the K shell, emitting K radiation. The vacant space left in the L shell is filled by an electron from the M shell, emitting the L radiation. Thus, an atom can emit x-rays having a series of different wavelengths almost simultaneously. These fluorescent x-rays are characteristic of the fluorescing atom, and the element can be identified from the wavelength of the fluorescent ray and determined in a mixture from the intensity at the identified wavelength. Thus, x-ray fluorescence is atomic emission comparable to optical (ultraviolet or visible) emission. Analysis by means of x-ray fluorescence is frequently, and perhaps not quite properly, referred to as "x-ray emission analysis."

An x-ray fluorescent spectrometer consists of an x-ray tube capable of emitting an intense x-ray beam which impinges upon the sample to be analyzed. The fluorescent rays are dispersed by utilizing a crystal with a known lattice constant, frequently a bent mica crystal, which acts as a diffraction grating. The diffracted fluorescent x-rays are detected by a Geiger counter goniometer and their intensities automatically recorded as a function of the goniometer angle, which is proportional to the wavelength or frequency of the x-rays. A typical curve, obtained in the analysis of a chrome-nickel plating on silver-copper base, is shown in Figure 16. The position on the abscissa identifies the element, and the magnitude on the ordinate the concentration, by calibration with known standards.

X-ray fluorescence offers a potentially valuable adjunct to optical emission methods which have proved of considerable value in the analysis of various natural sources of fatty acids and their derivatives, as in the quantitative determination of trace metals causing increased rancidity in vegetable oils, which is described in a later section. X-ray fluorescent spectra are usually considerably simpler than optical spectra. A sample containing a major portion of iron and/or manganese, for example, in

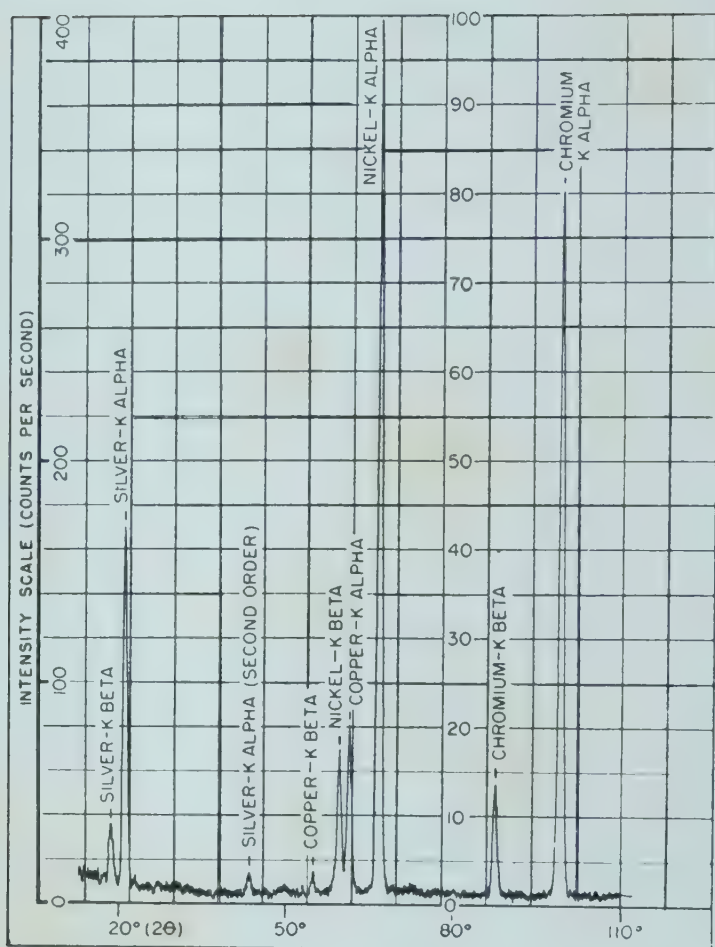


Fig. 16. X-ray fluorescent spectra of a chromium-nickel plating on a silver-copper base (16a).

optical emission exhibits spectra which consist of several hundreds of iron and manganese lines arising from the many possible transitions of the valence electrons of these two elements. From this myriad of iron and/or manganese lines, the lines of the trace metals sought must be distinguished. X-ray spectra will, usually, consist of only one to four lines representing the electron transitions from the K and L radiations. Qualitative analysis is, therefore, considerably easier; and quantitative analysis, because of the less possibility of interferences, is more certain. The rapid introduction of x-ray fluorescent spectrophotometry has been accompanied by considerable interest in the use of this tool in the metal

industries. Its potential use in the analysis of fatty acid derivatives and natural sources of them, particularly to complement optical emission methods, is quite obvious.

3. Ultraviolet

(a) Emission

All three types of radiation in the ultraviolet portion of the electromagnetic spectrum—emission, absorption, and scattering—have been applied to the analysis of fatty materials. Emission spectroscopy is an atomic process used extensively for qualitative detection and quantitative determination of traces of the chemical elements, particularly metals. Its application to fatty acid chemistry is, therefore, more directed toward analysis of natural fats and oils or processed fats and oils rather than the fatty acids or simple glycerides. Markley and Goss (17) have commented that “in view of the fact that a few parts per million of copper salts (oleate) adversely affect the stability or keeping quality of most refined oils, it would be of interest to know how much of the total copper, contained in soybeans, finds its way into the refined oil.” Husaini and Saletore (18) reported on the effect of metals on vegetable oils, and Lea (19) has shown that extremely small concentrations of many metals may affect their keeping quality. The determination of residual traces of metals used in the catalytic hydrogenation of fats is another example of the application of emission spectroscopy in fatty acid chemistry (20).

When the atoms of any substance are excited, as by a flame, electric arc, or spark, some of the heat or electrical energy may be absorbed as electronic energy. Atoms in the ground state are raised to the first excited level (arc spectra) or atoms in lower excited states are raised to higher excited states (spark spectra.) When these atoms return either to less excited states or to their normal unexcited ground state, this energy is given off as electromagnetic radiation, the wavelength of which, in accordance with the quantum equation, will depend upon the difference in the energy between the two states. Any given atom has only certain discrete energy levels; hence it can radiate only at certain frequencies. The wavelength of the lines observed in an emission spectrum can, therefore, be correlated with particular elements either by exact wavelength measurements and comparisons with standard tables, such as the very complete compilation of Harrison (21), or they can be identified by direct comparisons with the known spectra of specific elements. The latter technique is more commonly used in the chemical spectroscopy laboratory. In

either technique a qualitative method of analysis for the elements is achieved. Careful measurement of the intensities of identified lines, obtained under standardized conditions of excitation and measured by analytically reproducible techniques, permits the process to be made quantitative. The method is particularly useful for the identification and determination of metals in concentrations as small as one part in 10 million or, in some cases, one part in 100 million. At concentrations of about 1% the classical wet methods of chemical analysis begin to become competitive and much above this concentration they are usually superior in precision and accuracy to spectroscopic methods.

While direct methods of spectroscopic analysis for traces of metals are available, these are generally practical only in large-scale analyses, as in metallurgical applications. More commonly used in research or control laboratories are the photographic methods. Using suitable sensitized photographic plates, which are commercially available, it is possible to photograph to about 2000 Å., i.e., to the edge of the vacuum region where the absorption by air makes further measurements impossible without elaborate vacuum spectrographs. An example of the use of these short wavelengths for emission analysis has been given by O'Connor (22) for the determination of zinc.

O'Connor *et al.* (23) have described in detail a method for the preparation of ash for the determination of traces of metallic elements in oils, fats, and related substances, and subsequently (24) an application of the line-width technique to the analysis of these substances, together with a discussion of the precision and accuracy that may be expected.

Evans *et al.* (25) used spectrochemical methods to determine the copper and iron content of several soybean oils in their studies of the effect of these metals on the stability of oils. In connection with their studies of the flavor changes of soybean oil, Evans *et al.* (26) also applied spectrochemical methods to determine the content of copper and iron prior to and following various steps of processing these oils. Melvin and Hawley (27), using a modification of the ashing technique of O'Connor *et al.* (23), were able to determine copper and iron content of corn and soybean oils to sensitivities of 0.001 p.p.m. for copper and 0.01 p.p.m. for iron.

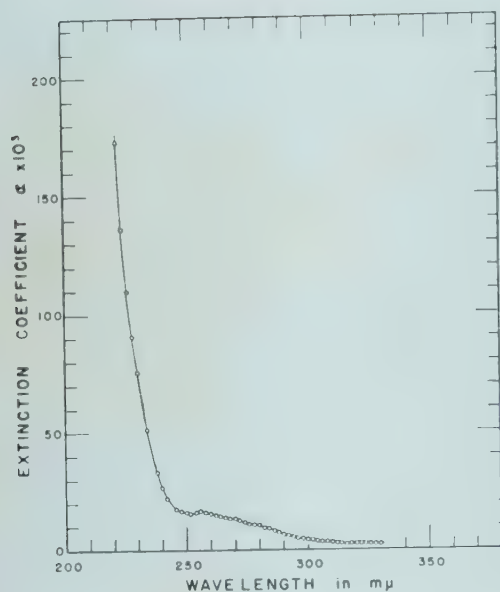
(b) Absorption

The lower limit of ultraviolet spectra is at the edge of the x-ray region (Fig. 14) or about 20 Å., but a further limitation of instrumentation restricts the practical application of ultraviolet absorption to about 200

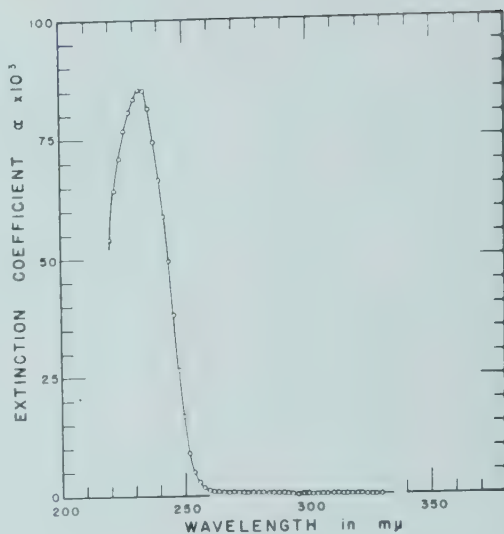
m μ . Several factors contribute to this limitation, namely: (a) quartz, the usual material for optics in the ultraviolet region, begins to absorb; (b) the detectors, i.e., photoelectric cells, become less sensitive; (c) the light sources, i.e., the hydrogen discharge lamp, become weaker; and (d) air soon begins to absorb radiation and a complete vacuum is required. Vacuum spectrophotometers, which employ gratings to avoid the absorption occurring with quartz optics and special types of detectors sensitive to short wavelength ultraviolet radiation, have been designed to permit measurements particularly in the region of ethylenic absorption or about 170 to 200 m μ . The usable ultraviolet absorption region for chemical spectroscopy of fatty acids may be considered to be from 200 to 400 m μ . Rusoff *et al.* (28) reported ultraviolet spectra for several fatty acids and related compounds down to 170 m μ , and this region must be considered as potentially useful for detection of such groups as the single ethylenic linkage (—C=C—) and the carboxyl (—COOH), especially now that vacuum spectrophotometers are commercially available.

If a chemical compound is subjected to radiation of progressively changing wavelengths, it may absorb any portion of this radiation whose energy is exactly equal to the energy difference, ΔE , between two of the electronic levels within the molecule. The absorption process is molecular in nature and usually involves changes in electronic, and simultaneously, in vibrational and rotational levels, as explained earlier. Absorption processes can occur in elements, but in application to chemical analysis, molecular absorption is far more important, and it only has had application to the analysis of fatty acid materials. In Figure 17 two general types of absorption are illustrated. Nonselective or noncharacteristic absorption (Figs. 17a and 17c) are examples where the particular molecule possesses no electronic levels whose energy difference corresponds exactly to any of the energy of the radiation falling upon it. The observed smooth absorption, which generally increases toward the shorter ultraviolet, is caused by end absorption of very intense bands in the far (vacuum) ultraviolet region. This type of absorption is of little or no importance to chemical spectroscopy.

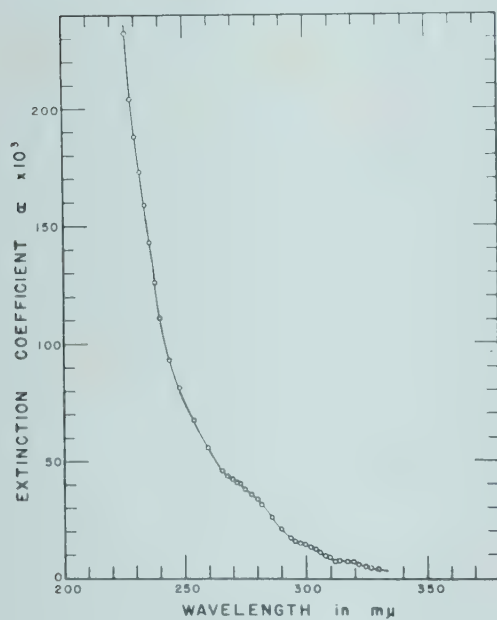
The second type of absorption, consisting of specific maximum and minimum, is illustrated in Figures 17b and 17d. The wavelength position of such characteristic absorption may be correlated with specific types of molecules and used as a means of qualitative identification. The intensities of these bands, by comparison with the intensities of known pure compounds, provide a means of quantitative analysis. Applications of ultraviolet absorption spectroscopy to chemical analysis is limited to those



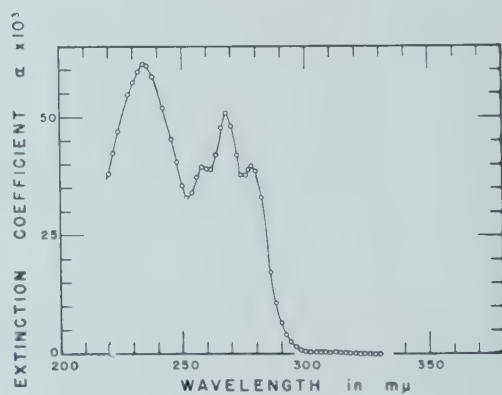
(a)



(b)



(c)



(d)

Fig. 17. Ultraviolet absorption spectra (29); (a) and (c) linoleic and linolenic acids, respectively; (b) and (d) alkali-isomerized linoleic and linolenic acids, respectively.

types of molecules which give rise to characteristic absorption in the region 200 to 400 $m\mu$. Fundamental studies have shown that such selective

absorption will occur in this region only for molecules having π (or unsaturated bond) electrons. Experience has verified the theoretical conclusions, and only unsaturated compounds exhibit characteristic absorption. However, not all unsaturated compounds give rise to characteristic bands in this region. This is illustrated in the spectra of very pure linoleic and linolenic acids (Figs. 17a and 17c). In spite of the fact that each of these molecules contains a carboxyl group and either two or three methylene groups, ($-\text{CH}=\text{CH}-$), only nonselective absorption is observed. As previously indicated, the explanation for this apparent nonselective absorption is that these groups exhibit their characteristic bands just below the limits of this region with maxima about 170 to 190 $\text{m}\mu$ (28). However, some molecules with isolated unsaturated groups do exhibit specific absorption between 200 and 400 $\text{m}\mu$, the most important example of which, in the case of aliphatic materials, is the carbonyl group

O
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($-\text{HC}=\text{O}$) of aldehydes and that of ketones, ($\text{R}-\text{C}-\text{R}$), which will be discussed later.

Conjugation of a single unsaturated linkage with a second unsaturated group gives rise to intense absorption bands throughout the region 200 to 400 $\text{m}\mu$. Conjugation of two ethylenic linkages, forming a conjugated dienoic system ($-\text{C}=\text{C}-\text{C}=\text{C}-$), gives rise in the absorption spectra of fatty acids and their derivatives to absorption bands of considerable intensity in the region about 230 $\text{m}\mu$, the exact position of which can be calculated by means of Woodward's rule. According to this rule, the position of maximal absorption of a normal diene can be calculated simply by adding 5 $\text{m}\mu$ to the position of the maximum for butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, (ca. 217 $\text{m}\mu$) for each substituent, and 5 $\text{m}\mu$ for each exocyclic bond present in the diene system. Extension of the conjugated system to a trienoic conjugation, $\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-$, results in a shift in the absorption to about 268 $\text{m}\mu$, while a tetraenoic system absorbs at about 315 $\text{m}\mu$, pentaenoic at about 346 $\text{m}\mu$, and hexenoic at about 374 $\text{m}\mu$. Further extension of the system of conjugated double bonds eventually leads to the formation of colored compounds and absorption into the visible region. In this region Hewitt's rule, known since 1907, applies. According to this rule, the longer the conjugated unsaturated system, the deeper will be the resultant color.

Although ultraviolet absorption of unconjugated unsaturated compounds has limited utility, examples of which will be given later, the greatest utility of this type of absorption, as well as visible absorption

spectroscopy, is limited to the study of compounds containing conjugated bonds. Observation of the ultraviolet spectrum of any fatty acid, ester, glyceride, or natural product from which these compounds are derived can answer such questions as: (a) Does the sample contain any unsaturated conjugated material? (b) If conjugated substances are present, what is the order of conjugation? (c) If there is evidence of diene conjugation, what does Woodward's rule imply about the nature of the substituents? (d) If triene conjugation is detected, is this conjugation in a single ring, i.e., is the material aromatic or aliphatic? (e) If diene conjugation involves a nonaromatic ring, what do the extensions of Woodward's rule imply concerning the possibility of the unsaturation being entirely within the ring, esocyclic on the ring, or exocyclic to it? It is apparent that any property of matter that can be utilized to answer such questions would find several applications in the field of fatty acid chemistry.

Quantitative Single-Component Analysis. Two laws that are important to the use of absorption spectra as a means of quantitative analysis are those of Bouguer and of Beer.

Bouguer's law states that the proportion of radiation absorbed by a transparent medium is independent of the intensity of the incident radiation and that each successive unit layer of the medium absorbs an equal fraction of the radiation passing through it, or expressed mathematically,

$$-dP/db = aP$$

Integrating over the thickness of the medium, b ,

$$\text{Log}_{10} P_0/P = ab$$

or,

$$a = A/b$$

Beer's law states that the light absorption is proportional to the number of molecules of the absorbing substance through which the light passes, or expressed mathematically

$$-dP/dc = aP; \text{Log}_{10} P_0/P = ac; a = A/c$$

These two laws can be combined into a single expression,

$$a = A/bc$$

If the absorbance of a material, A , is measured in a cell b cm. long, the concentration of the absorbing compound, c , in grams per liter, can be

calculated if a , the characteristic constant for this absorbing compound, is known, by means of the expression,

$$c = A/ab$$

The very simple determination of α -eleostearic acid in fresh tung oil affords an excellent illustration of a single component spectrophotometric quantitative determination (29). So-called α -tung oil owes its particular properties as a drying oil to the presence of large quantities (ca. 80%) of α -eleostearic acid, 9-*cis*,11-*trans*,13-*trans*-octadecatrienoic acid. This is a naturally conjugated trienoic acid and exhibits intense absorption in the ultraviolet region with a maximum at 271.5 $m\mu$ (Fig. 18). Estimations of the quality of tung oil have been made by long, tedious, and not entirely satisfactory determinations of eleostearic acid by empirical cal-

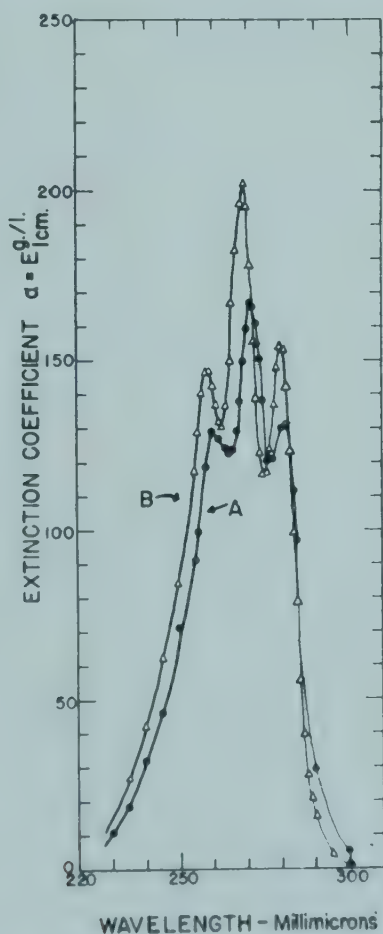


Fig. 18. Ultraviolet absorption spectra of α - and β -eleostearic acid; (A) α -eleostearic acid, (B) β -eleostearic acid (29a).

culations from maleic anhydride reactions. If a few drops of the oil are accurately weighed into a small volumetric flask, dissolved in cyclohexane, and brought to volume with the same solvent, a single spectrophotometric measurement at $271.5\text{ m}\mu$ will provide the data required to calculate the concentration of the eleostearic acid in the sample of tung oil from the Bouguer-Beer equation:

$$c = A/176.7 \times b$$

(176.7 is the absorptivity which has been established for cyclohexane solutions of α -eleostearic acid at its maximum at $271.5\text{ m}\mu$ when measured on the Beckman DU spectrophotometer at a slit width of 0.3–0.4 mm. (30). The analysis can be made in a few minutes instead of a day required by the maleic anhydride addition method. No other component of unisomerized tung oil contributes to the absorption at $271.5\text{ m}\mu$ and no corrections for interfering absorption are required.

Quantitative Multicomponent Analysis. As tung oil ages, its viscosity may increase and it may, under some conditions, become completely solid. The oil is then known as β -tung oil. This change is due, in large measure, to isomerization of α -eleostearic acid to the β -isomer. Two groups of workers (31,32), among others, applied infrared absorption spectroscopy to establish the molecular configuration of these two acids as 9-*cis*,11-*trans*,13-*trans*-octadecatrienoic and 9-*trans*,11-*trans*,13-*trans*-octadecatrienoic acids, respectively. The ultraviolet absorption of these two acids is similar, but not identical (Fig. 18). In an isomerized tung oil the relative proportions of the two isomeric components can be determined by the technique known as spectrophotometric multicomponent analysis. This determination requires a knowledge of the absorptivity of the α -isomer, preferably at a position of one of its maximum absorption bands, and the absorptivity of the β -eleostearic acid at this position; and it also requires a knowledge of the absorptivity of the β -isomer at one of its maxima where the absorptivity of α -eleostearic acid is known. These required constants have been evaluated for the Beckman Model DU spectrophotometer with a slit width between 0.3 and 0.4 mm. (30).

At $271.5\text{ m}\mu$ α -eleostearic acid (maximum); $a = 176.7$

β -eleostearic acid; $a = 168.0$

At $269.0\text{ m}\mu$ β -eleostearic acid (maximum); $a = 201.8$

α -eleostearic acid; $a = 157.3$

Therefore, at $271.5\text{ m}\mu$ the total measured absorptivity of the sample will be

$$176.7 \times \% \alpha\text{-acid} + 168.0 \times \% \beta\text{-acid}$$

and at 269.0 $m\mu$ the total measured absorptivity of the sample will be

$$201.8 \times \% \beta\text{-acid} + 157.3 \times \% \alpha\text{-acid}$$

Simultaneous solution of the two equations and spectrophotometric measurement and calculations of the two absorptivities of the sample at the two wavelengths permits a calculation of both α - and β -eleostearic acid in any given sample.

The foregoing are illustrative examples of a single component and a multicomponent spectrophotometric analysis of a fatty acid material.

From Figure 18 it can be seen that the absorptivity curves cross at, for example, 276.8 $m\mu$. At this point the total absorption is independent of the ratio of α - and β -isomers. Such an absorption position is called an "isobestic point." It can be used as a direct determination of total eleostearic acid to check the sum of the α - plus the β -acids obtained from the simultaneous equations. The absorptivity at this isobestic point has been established (30) as 123.7; therefore,

$$\text{Total eleostearic acid} = A/123.7 \times b$$

The general method of multicomponent analysis can be extended, with increasing mathematical complexity, to three, four, five, or more components, all of which must exhibit selective absorption with maxima at well-resolved wavelengths.

Ultraviolet spectrophotometry provides not only a much more rapid determination of eleostearic acid content in tung oil than is possible by chemical methods, but also it affords as simple a means for determining the relative proportion of the two isomers, an analysis which cannot be done by chemical means. This latter determination may be of considerable importance in industrial storage of tung oil.

Quantitative Determination of Nonconjugated Acids. The polyunsaturated constituents of most fats and oils are nonconjugated and they therefore exhibit spectra similar to those of linoleic and linolenic acids (Fig. 17a and 17c); hence they are not amenable to spectrophotometric analysis. Dann and Moore (33) and Moore (34) showed that linoleic and linolenic acids are isomerized respectively to conjugated dienoic and mixtures of conjugated dienoic and trienoic acids by heating with alcoholic potassium hydroxide (Figs. 17b and 17d). Kass *et al.* (35) showed that this isomerization is effected much more rapidly at higher temperatures, i.e., with the use of a solution of alcoholic potassium hydroxide and ethylene

glycol at 180°C. Mitchell *et al.* (36) applied this procedure to establish a quantitative spectrophotometric method for the determination of the content of the linoleic and linolenic acid components of a fat.

Since the method was first described by Mitchell *et al.* (36) in 1943 it has undergone various modifications and extensions, and has been applied to numerous natural and synthetic products. In 1945, Brice *et al.* (37,38) applied the method to the determination of arachidonic acid, using absorptivity values proposed by Beadle and Kraybill (39). Later, it was extended by Herb and Riemenschneider (40) to include pentaenoic acid; Hammond and Lundberg (41) suggested its application to the hexaenoic acids.

The early applications of the spectrophotometric method for determining polyunsaturated acids were confused by the presence in many natural fats and oils of "preformed" conjugated acids, as was evident by the observation in the unisomerized products of absorption bands characteristic of dienoic conjugation at 232 m μ , of trienoic conjugation at 268 m μ , and in some cases of tetraenoic conjugation at 316 m μ . This preformed conjugation was believed to arise from conjugation of linoleic, linolenic, and arachidonic acids during the extraction or subsequent treatment of the oil. The spectra of several vegetable oils, after alkali isomerization, exhibited traces of trienoic absorption, although from chemical evidence these oils, namely, cottonseed, peanut, sesame, etc., were assumed to contain no linolenic acid. Similarly, the spectra of some semidrying and drying oils (soybean, linseed) exhibited traces of tetraenoic acids, although such acids were assumed to occur only in animal and fish oils. The detection in vegetable oils of such polyenoic acids by spectrophotometric but not by chemical methods was attributed to the insensitivity of the latter methods.

O'Connor *et al.* (42) demonstrated that linoleic and linolenic acids were highly susceptible to oxidation which subsequently led to the formation of conjugated isomers of the next higher order, i.e., trienoic from linoleic acid and tetraenoic from linolenic acid. Hilditch *et al.* (43) questioned the validity of associating this conjugation absorption with the presence of the higher polyenoic fatty acids, and Swift *et al.* (44), in their investigation of the oxidation products of cottonseed oil, concluded that this absorption most probably arose from the presence of α,β -unsaturated aldehydes and dienals which exhibit characteristic absorption at about the wavelengths characteristic of the polyenoic acids. This evidence, linking preformed conjugation with oxidation processes, led Swain and Brice (45) to a detailed reinvestigation of the formation of such constituents. They demon-

strated that traces of conjugation absorption arise from autoxidation products of oleic, linoleic, and linolenic acids, and they proposed tests by means of which true isomers of unsaturated fatty acids could be distinguished from such autoxidation products. Preformed conjugation is now regarded as a measure of the extent of autoxidation of an oil, rather than evidence of the presence of conjugated acids.

Several modifications of the method of Mitchell *et al.* (36) were proposed to improve its precision and accuracy. O'Connor *et al.* (46) applied the method to determine the proportion of soybean oil admixed with cottonseed oil by measuring the trienoic conjugation arising from the presence of linolenic acid in the former oil. These investigators resorted to blanketing of the oil with nitrogen during isomerization and also during the preparation of the reagent in order to avoid alteration of the readily oxidizable components. Brice and co-workers (37,38) introduced mathematical equations to correct for "background" absorption when applying the method to the quantitative detection of very small quantities of linoleic, linolenic, and arachidonic acids in animal fats. These corrections, while valuable when measuring quantities of 1% or less of unsaturated constituents, involve unnecessary expenditures of time and effort, and are undesirable in the analysis of most vegetable and drying oils, where concentration of the acid components is of the order of 20 to 50%.

Hilditch and co-workers (47) described two different modifications of alkali isomerization, one ideal for linoleic and the other for linolenic acid, and somewhat later Vandenheuvel and Richardson (48) described an entirely new procedure of alkali isomerization. Brice *et al.* (49) pointed out that natural oils subjected to spectrophotometric analysis contained fatty acids in the *cis*-form, whereas the absorption constants used in calculating the results were derived from acids prepared by bromination-debromination, which leads to a mixture of *cis*- and *trans*-isomers. They used pure *cis*-linoleic, linolenic, and arachidonic acids prepared by physical methods (50,51) from natural sources to obtain new spectrophotometric constants, the application of which led to improved accuracy of the analytical results. However, even when the new constants were applied with hydrogenated fats, discrepancies were still reported (52-54).

Work of Riemenschneider *et al.* (50) and of Nichols *et al.* (55,56) demonstrated that the rate of isomerization and the magnitude of the absorptivities obtained varied for *cis,cis*-, *cis,trans*-, and *trans,trans*-acids. The accuracy of the method based on standards for *cis*-acids is, therefore, not satisfactory for the analysis of partially hydrogenated products which are known to contain mixtures of *cis*- and *trans*-acids. Brice *et al.* (49)

showed that concordant results can be obtained by the spectrophotometric method when analyzing products containing only *cis* components. O'Connor *et al.* (57) made a detailed comparison of the spectrophotometric and chemical methods for the analysis of a number of cottonseed oils and showed good agreement between the two. Baldwin and Longenecker (58) verified the validity of the spectrophotometric method by the analysis of known mixtures of purified methyl esters, as did Baldwin and Daubert (59) with the analysis of synthetic glycerides.

The present Official Method Cd 7-58 (60) of the American Oil Chemists' Society for the determination of polyunsaturated acids is a considerably revised and expanded modification of the method of Mitchell *et al.* (36) and is the result of many collaborative investigations by the Spectroscopy Committee. Between 1952 and 1956 the AOCS Spectroscopy Committee (61) recommended revisions leading to a method applicable to the determination of linoleic, linolenic, arachidonic, and pentaenoic acids. The method includes the use of (a) the "background" corrections proposed by Brice *et al.* (37,38) only if traces of the unsaturated acids are being determined; (b) protection by nitrogen blanketing recommended by O'Connor *et al.* (46); (c) constants for natural acids proposed by Brice *et al.* (49); and (d) simplifications of the technique when the materials being analyzed do not contain all of the polyunsaturated acids, e.g., cottonseed oil which contains only diene unsaturation (linoleic acid) is determinable by a single measurement at 233 m μ . The Spectroscopy Committee tested and confirmed the reliability of the method in collaborative studies and concluded that reasonable reproducibility can be obtained by experienced operators (61). The two most serious limitations of the method are difficulties in analyzing products which contain large proportions of preformed conjugation, e.g., tung oil which contains about 80% of the triene-conjugated eleostearic acid, and also inability to obtain accurate results with products containing *trans*-acids. A method for the determination of linoleic acid in tung oil and similar materials was proposed by O'Connor *et al.* (62) in 1953 and submitted to the Spectroscopy Committee for further investigation. Jackson *et al.* (63) confirmed the results of Riemenschneider *et al.* (50) and Nichols *et al.* (55,56) regarding the rate of isomerization of *cis*- and *trans*-isomers. They showed that of three nonconjugated isomeric linoleic acids, the *cis,cis*-isomer reaches a maximum value of conjugated absorption upon alkali isomerization very rapidly; the *trans,trans*-isomer very much more slowly; and the *cis,trans*-isomer is intermediate between the other two. Furthermore, they observed that after isomerization for 285 minutes all three isomers reach

the same value of absorptivity. Consequently, a mixture of *cis,trans*-isomers, after alkali isomerization for 285 minutes, can be analyzed for total linoleic acid by making a single measurement at the appropriate wavelength. Jackson *et al.* (63) showed how advantage may be taken of the different rates at which this constant value of absorptivity is reached to determine approximately the concentrations of the three isomers. Methods for the determination of the proportion of *cis*- and *trans*-acids by means of infrared absorption may lead to a procedure whereby such mixtures can be analyzed much more rapidly.

A variety of applications of the alkali isomerization-ultraviolet spectrophotometric method has been described. Among others, these include the determination of soybean oil in admixtures with cottonseed and other oils containing little or no linolenic acid; the detection (64-66) of adulteration of ground beef, pork, or lamb with horsemeat; the detection (67) of adulteration of commercial corn oil with soybean oil; the differentiation of butterfats from margarine fats; and the detection (68) of lard in hydrogenated vegetable oils. The introduction of a microtechnique by Herb and Riemenschneider (69) has proven particularly useful in medical, biochemical, and other applications where the amount of material available for analysis is limited.

Collins and Sedgwick (69a) described a simplification of the AOCS procedure which permits the routine analysis of 60 samples per day of soybean oil for linoleic and linolenic acids. Birch *et al.* (69b) suggested the use of potassium amide in liquid ammonia for alkali isomerization and Davanport (69c) reported a preliminary investigation of the use of potassium *tert*-butoxide in *tert*-butanol. Sreenivasan and Brown (69d) described, in more detail, the use of the latter reagent for the isomerization of linoleic, linolenic, and other polyunsaturated acids, and its application in the spectrophotometric estimation of these acids.

Among the various reviews on the alkali isomerization-ultraviolet absorption method may be mentioned those of O'Connor (29), Beadle (70), and Herb (71) which the reader may wish to consult.

Investigations of Oxidation. Reference was made earlier to unsaturated nonconjugated groups which exhibit low-magnitude selective absorption in the ultraviolet region of the spectrum. Among the more important configurations responsible for such absorption in compounds related to the fatty acids is the carbonyl linkage, $C=O$. The carbonyl group of aldehydes and ketones, but not of acids or esters, gives rise to low, broad characteristic absorption bands between about 265 and 285 $m\mu$. The appearance of such bands in the spectra of fatty acids or esters, in association

with other changes, e.g., changes in viscosity, peroxide value, etc., is indicative of the occurrence of oxidation, and measurement of the intensity of this absorption can be used to estimate the extent of the oxidation. When the carbonyl group is conjugated to ethylenic linkage(s), conjugated absorption in the diene, triene, tetraene, etc., regions is produced. Ultraviolet absorption studies involving these groups have been useful in investigating autoxidation of vegetable oils, siccative processes, development of color, and factors affecting rancidity.

Mitchell and Kraybill (72) observed that bleaching oils with fuller's earth caused the development of specific absorption bands in the spectra of the bleached oils. Bleaching oils containing linoleic acid were accompanied by the formation of absorption bands at $268\text{ m}\mu$, the trienoic region; and oils containing both linoleic and linolenic acids developed bands at 268 and $316\text{ m}\mu$, i.e., in the regions of the triene and tetraene absorption. These authors assumed that the formation of such conjugated systems resulted from oxidation of double bonds followed by dehydration of the oxidation products. O'Connor *et al.* (42) showed that unless pure linoleic and linolenic acids are protected from oxidation, e.g., under an atmosphere of nitrogen, conjugation absorptions of the next higher order, i.e., triene from the linoleic acid and tetraene from the linolenic acid, will appear in the ultraviolet spectra.

Mitchell and Kraybill (73) compared the ultraviolet absorption spectra of linseed oils heat-bodied *in vacuo* at 307°C . and blown (oxidized) at 104.4°C . Only the blown oil exhibited characteristic bands in the region 260 to $270\text{ m}\mu$. It was suggested that these bands be used to distinguish between vacuum-polymerized and oxidized linseed oils in mixtures with raw linseed oil. The absorptivity at $232\text{ m}\mu$ may be used for the quantitative determination of oxidized or heat-bodied linseed oil in admixture with raw linseed oil.

Holman and co-workers studied the ultraviolet absorption of pure and oxidized monoethenoic acids and esters (74), octadecadienoic acids (75), and octadecatrienoic acids (76). They found that oxidation of monoethenoic acids led to increased absorption at $235\text{ m}\mu$, indicating to the authors the probable formation of conjugated dienes. Oxidation of the dienoic compounds was accompanied by increased absorption at $275\text{ m}\mu$, not directly related to the formation of peroxides, while oxidation of non-conjugated trienes was accompanied by increase in absorption at 235 and $275\text{ m}\mu$. Oxidation of conjugated linoleic acid greatly reduced the absorption at $233\text{ m}\mu$, and oxidation of conjugated trienes was accompanied by a decreased absorption in the region of 260 to $280\text{ m}\mu$ and increased

absorption in the regions of 230 and 320 $m\mu$. Cold alkali had no effect upon the absorption of the freshly prepared conjugated or unconjugated acids, but produced marked changes in the oxidized products; therefore they concluded that the absorption bands which accompany autoxidation result from the formation of oxygen-containing chromophores. It was suggested that the increased absorption observed in the spectra of oxidized fats is due, in part, to the formation of conjugated unsaturated systems containing carbonyl groups, or to conjugated polyenes formed by enolization.

Holman and Burr (77) made similar studies of lipoxidase oxidation of natural fats. Swift *et al.* (44) showed that the oxidation products of methyl oleate and of cottonseed oil included α,β -unsaturated aldehydes and dienals which absorb selectively in the region of diene and triene conjugation. They attributed the absorption to conjugation of the carbonyl and ethylenic linkages. Swain and Brice (45) concluded that the appearance of trienoic and tetraenoic conjugation observed in the ultraviolet spectra of several alkali-isomerized vegetable oils had its origin in oxidation products of linoleic and linolenic acids.

Wolff (78) examined the ultraviolet absorption spectra of natural oils which had undergone oxidation. The absorption at 232 $m\mu$ of almond, peanut, and olive oils, and pure linoleic acid increased with the increase of the peroxide values of these substances. Unlike ethyl linoleate, the absorption of the oils also increased at 270 $m\mu$. The first absorption, at 232 $m\mu$, was considered to arise from the formation of hydroperoxides, and that at 270 $m\mu$ from ketonic oxidation, probably to form diketones. Bleaching clay (Clarsil) caused increased absorption at 270 $m\mu$ and a decrease at 232 $m\mu$, which was attributed to decomposition by the clay of the linoleate hydroperoxides and formation of unsaturated systems with four double bonds. However, if tetraenoic conjugation occurred, it would be expected to increase the absorption at about 315 $m\mu$ and not at 270 $m\mu$ in the triene region. The nonvolatile oxidation products in crude oils persist in some type of transformation product in the refined oils; hence Wolff concluded that ketonic compounds are, from the practical point of view, not eliminated by refining and that it cannot be hoped to obtain high-quality refined products from poor grades of crude oils.

Wolff (79) also applied ultraviolet spectrophotometry in an investigation of the air-oxidation of linseed oil at various temperatures. His results indicated that hydroperoxides are formed at low temperatures and subsequently undergo decomposition to secondary oxidation products at higher temperatures. Wolff suggested that the ratios of the absorptivities

at 232 and 270 $m\mu$ could be employed to (a) differentiate stand oil from boiled oil; (b) estimate the proportion of boiled oil in stand oil; and (c) distinguish extracted oil, which is heated to expel solvent, from crude pressed oil. Treatment of oxidized oil with decolorizing earth increased absorption at 270 $m\mu$ and decreased it at 232 $m\mu$. At 150° C. this treatment produced absorption at 303 and 317 $m\mu$ without changes at 232 or 270 $m\mu$. Wolff also showed that rancidity in linoleates, oleates, and olive, peanut, and almond oils can be detected spectrophotometrically by the formation of conjugated double bonds (80).

Wekua and Bergmann (81) used ultraviolet absorption to study synthetic drying oils. Using spectrophotometric analysis, Vaillant (82) demonstrated that during initial stages of the "standolization" of linseed oil, linoleic acid disappeared (reacted) more rapidly than linolenic acid. At a viscosity of 1 poise, linolenic acid reacted 7 times as rapidly as linoleic acid, but above 60 poises the reaction velocity was the same for both acids.

Lundberg *et al.* (83) reported absorption spectra corresponding to different stages of oxidative deterioration (rancidification) of lard, and ethyl oleate and linoleate. Hendrickson *et al.* (84) concluded from the results of ultraviolet spectrophotometric investigations of drying oils that drying (autoxidation) and film formation proceeds in three stages, namely, (a) a short, initial stage characterized by an accumulation of conjugated diene and triene structures and possibly an increase in enolizable α -keto groups, evidenced by absorption maxima characteristic of triene and tetraene conjugated systems; (b) a slow decrease in the measurable conjugated diene and triene structures; and (c) a third and final deterioration stage. The principle, that the quantity of light absorbed by an oil film in the region 320 to 400 $m\mu$ is indicative of the durability of the film upon exposure to accelerated weathering conditions, was verified. Ultraviolet spectrophotometry, it was concluded, "is a valuable tool for investigating some of the chemical changes which occur as a vegetable oil film dries and ages."

Japanese workers have also reported studies on the oxidation of fatty acids, particularly higher polyunsaturated acids, by means of ultraviolet spectrophotometry. Toyama (85) summarized his work with several colleagues on the oxidation of pure acids with different reagents. In these studies they investigated the ultraviolet absorption spectra of the acids before and after alkali isomerization, and the products of oxidation and scission.

Several reviews describing the application of ultraviolet absorption spectra to drying oil chemistry have been published, among which may be mentioned those of Kass (85a) and Ahlers (86,87).

Determination of Vitamins. Vitamin A exhibits an ultraviolet absorption spectrum with a characteristic maximum at 328 $m\mu$ which can be used for the spectrophotometric determination of this vitamin (Fig. 19).

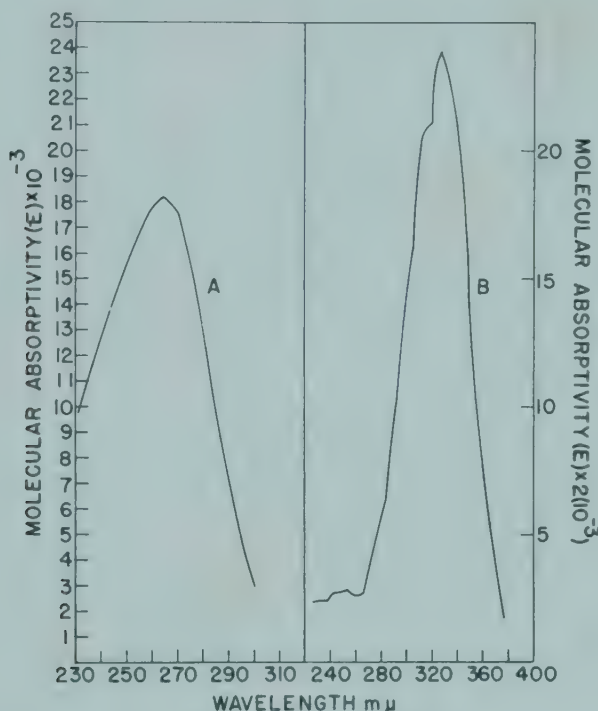


Fig. 19. Ultraviolet spectra of (A) vitamin D and (B) vitamin A.

From the absorption spectra of certain fish oils the presence of vitamin A can readily be detected by the appearance of this band. Tsuchiya and Kaneko (88) found that the spectra of 13 viscerol and 10 liver oils from 17 species of Japanese fish exhibited the absorption band at 328 $m\mu$, indicative of the presence of vitamin A. Similarly, Kamath and Magar (89) observed that 10 liver oils from 6 different species of Indian sharks exhibited characteristic spectra similar to that of a cottonseed oil to which vitamin A had been added.

The determination of vitamin A requires the extraction of the vitamin, measurement of the absorption of the extract at 328 $m\mu$, and applying to the observed value a mathematical correction. Morton and Stubbs (90) proposed to correct mathematically for extraneous absorption on the as-

sumption that when plotted, this extraneous absorption is a straight line across the portion of the spectral curve being examined. This method, which has been adopted by the U.S. Pharmacopeia (91) and the Association of Official Agricultural Chemists (92), has been shown to give good agreement with bioassay values of animal oils. Details of the procedure are found in the *Methods of Vitamin Assay* of the Association of Vitamin Chemists (93). Braekkan and Lambertsen (94) used the direct measurement of ultraviolet absorption with the Morton and Stubbs correction to determine vitamin A in cod-liver and other oils.

Luckman *et al.* (95) reported extensive studies of the ultraviolet absorption method for the determination of vitamin A in fortified fats, particularly margarine and various vitamin A concentrates. They used the unfortified material to determine the amount of "background" correction for extraneous absorption. Determinations of vitamin A were made by measuring the absorption of both the fortified and the unfortified samples at 328 m μ . The content of vitamin A of the fortified sample was then calculated from the relation:

$$\text{U.S.P. units of vitamin A per gram} = (a' - a) \times 5700 \times 1/0.3$$

where a' and a are absorptivities at 328 m μ , respectively, for the fortified and unfortified samples, 5700 is a factor for conversion from spectrophotometric to gravimetric units, and 0.3 is a factor to convert grams to U.S.P. units. Murray *et al.* (96) applied this technique to show that vitamin A was reasonably stable in sesame oil.

The method of Luckman *et al.* for the determination of vitamin A in margarine is ideal if a sample of unfortified product is available. Otherwise, recourse must be had, usually, to mathematical corrections for interfering absorption, which is a less satisfactory procedure. Several workers applied chromatography for the removal of the substances producing the interfering absorption prior to spectrophotometric measurement. Wilkie (97) used magnesia to purify extracts of margarine, but subsequent tests of his method revealed that the resulting extract does not exhibit a spectrum typical of vitamin A (102). Boldingh and Drost (98) used a twin chromatographic column, the upper one of which contained alumina and the lower one, alkali-treated alumina. They obtained an eluate which gave an absorption spectrum identical with that of pure vitamin A. Their method was studied by the Association of Official Agricultural Chemists for the determination of vitamin A in margarine (99) and it was made an official procedure in England (100). Braekkan and Lambertsen (101) simplified the procedure of Boldingh and

Drost (98) by combining the two adsorbents into a single column and claimed that it led to comparable results. Rosner and Kan (102) maintained that the use of alkali-treated alumina alone was sufficient. Lord and Bradley (103) opposed the use of specially activated unstable adsorbents and urged the use of natural bone meal with the method of Boldingh and Drost. However, the use of a natural product has likewise been criticized (103a) because of its failure to yield reproducible results.

It may be concluded that the method of Boldingh and Drost (98), or some modification thereof, is the most satisfactory procedure available for the determination of vitamin A in fortified margarines where the unfortified sample is not available. If the unfortified product is available, the procedure of Luckman *et al.* (95) is recommended. Morton and Bro-Rasmussen (104) have shown that in the analysis of certain natural products, particularly fish oils, for vitamin A, the problem is complicated by the presence of three vitamin A-active substances, all *trans*-vitamin A, neovitamin A₁, and vitamin A₂, all three of which have markedly different biological vitamin A potency. Bro-Rasmussen *et al.* (105) proposed a method involving a chromatographic separation of the three components on dicalcium phosphate columns and determination of each component by ultraviolet spectrophotometry. They illustrated their procedure by applying it to the analysis of fish oils, particularly cod-liver oil.

The ultraviolet spectrum of vitamin D is characterized by a band with an absorption maximum at 265 m μ (Fig. 19). This characteristic band can be used to detect and quantitatively to determine vitamin D in natural or irradiated fats and oils; like vitamin A, the shape of the absorption curve obtained with any extract of vitamin D is a valuable criteria of purity because any distortion of this curve reveals the presence of impurities. Brockmann (106) and Brockmann and Busee (107) have shown that vitamin D₂ (irradiated ergosterol) and vitamin D₃ (activated 7-dehydrocholesterol) have the same absorption curves and identical absorptivities. Reerink and van Wijk (108), Topelman and Schuhknecht (109), and Ol'khin (110) used the band at 265 m μ for a direct ultraviolet estimation of vitamin D₂ content.

The most frequently encountered interfering absorption at 265 m μ with extracts of vitamin D arises from the presence in the extracts of vitamin A, provitamin A (carotene), and related carotenoids, and from sterols. Marcussen (111) used Hydriffin K₄ and Ewing and co-workers (112) Superfiltrol as adsorbents in a chromatographic purification of vitamin D extracted from irradiated corn oil and fish-liver oils prior to

measurement of the ultraviolet absorption at 265 $m\mu$. Later, Ewing *et al.* (113) proposed a two-step, chromatographic purification process, the first step using Superfiltrol, the second, activated alumina. Satisfactory results were reported for the analysis of irradiated ergosterol in corn oil, crystalline vitamin D₂ and vitamin A acetate in corn oil, irradiated ergosterol and vitamin A palmitate in corn oil, fish-liver oils, and other products.

Miscellaneous Applications. The ultraviolet spectra obtained with several vegetable oils following various stages of processing have been discussed by O'Connor *et al.* (114,115). The significant absorption bands observed in the spectra of these oils were correlated with the compounds giving rise to them, and also with the chemical changes occurring during refining, bleaching, and deodorizing. Tsuchiya and Kaneko (88) similarly studied the ultraviolet spectra of several oils of Japan and discussed the absorption bands which were obtained with these lesser known oils. Uzzan (116) and Wolff (116a) pointed out the value of the use of ultraviolet absorption spectra in studies with olive and mixtures of almond and olive oils.

The ultraviolet spectrum of sesame oil (Fig. 20) differs from that of other well-known vegetable oils owing to the presence in the former of sesamin, sesamol, and sesamol. The ultraviolet spectra of pure samples of each of these components are shown in Figure 20. Sesamin is of

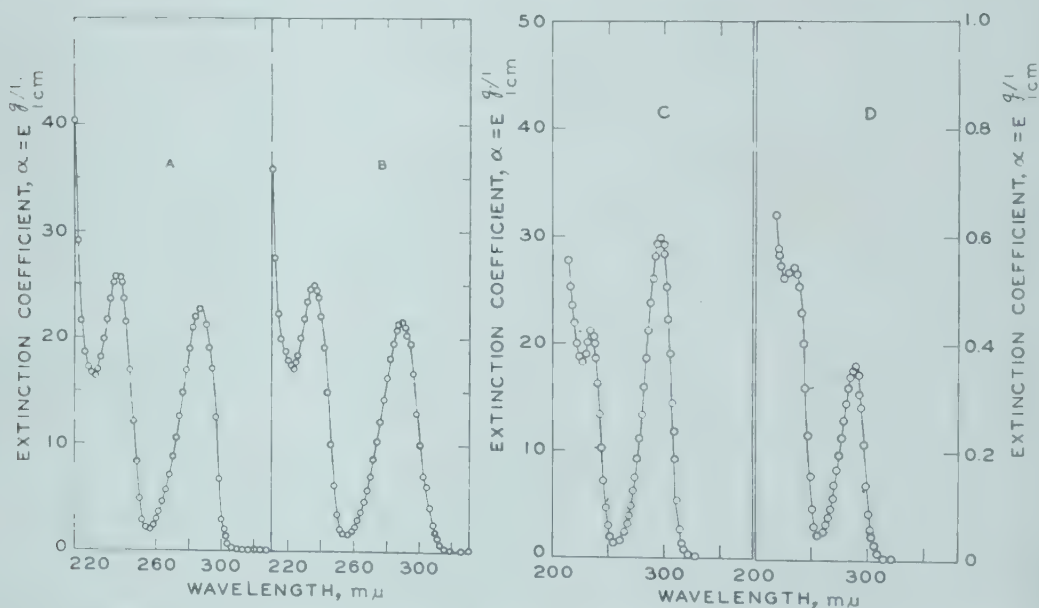


Fig. 20. Ultraviolet absorption spectra of (A) sesamin, (B) sesamol, (C) sesamol, and (D) crude sesame oil (117).

interest and commercial value because of its synergistic action in formulations of pyrethrin insecticides. Sesamolin and sesamol are antioxidants to which sesame oil owes its remarkable stability toward autoxidation. Budowski *et al.* (117,118) combined spectroscopy and the Villavecchia color reaction to determine simultaneously these three constituents by the multicomponent method of ultraviolet spectrophotometry. Suarez *et al.* (119) modified the method and extended it to sesamin concentrates. Beroza (120) incorporated in the method a chromatographic purification step using a silicic acid column, which is recommended particularly for products requiring large corrections for interfering absorption, e.g., oxidized sesame oils or oils previously subjected to some form of alkali isomerization.

4. Visible

(a) Emission—Flame Photometry

The methods of emission analysis used in the ultraviolet region of the electromagnetic spectrum can be extended, without any particular modification, to measurements in the visible portion. The alkali elements of the first group of the periodic table and, to a somewhat lesser degree, the alkaline earths of the second group have their most sensitive atomic spectral lines in the visible region. These sensitive lines, e.g., the D lines of sodium and the red lines of potassium, are easily excited and excitation can be produced by a flame instead of the higher energy electric arc. The high sensitivity of these lines is also favorable to the use of flame photometers where the intensities of the selected lines are read from a potentiometer. One advantage of the flame source, particularly for the determination of sodium and potassium, is that excitation is produced by a much lower source of energy; hence the number of interfering lines from other elements is considerably less. Qualitative identification is easier and the resolution of the various lines is considerably less stringent. For these reasons flame photometers are commonly used in the analysis for sodium and potassium. Because the entire spectrum of the sample is not obtained, it is imperative that independent evidence be obtained that there are no other elements present that might produce atomic lines which directly interfere with the reading of the selected line of the element being measured. This is particularly important in the use of flame photometers because these instruments generally do not permit very high resolution. Cox (121) reviewed the use of flame photometry in the analysis of paint and control in its manufacture.

(b) Absorption

Pure aliphatic acids, esters, and glycerides are colorless substances and do not exhibit absorption in the visible range of the electromagnetic spectrum. Natural fats and oils expressed or extracted from plant and animal organs contain varying amounts of pigments exhibiting visible absorption. It is possible, therefore, in many instances to measure the quantity of these substances by spectrophotometric methods. Gossypol, the principal pigment of cottonseed, can, for example, be determined by a direct spectrophotometric measurement of the absorption maximum at $368\text{ m}\mu$ in the band which is responsible for the yellow color of this pigment. In 1954 Stillman (122) proposed a method for the quantitative determination of chlorophyll and/or its degradation products in fats and oils by means of visible absorption. Other pigment, such as carotenes, carotenoids, flavones, etc., can also be determined by direct spectrophotometric measurement in the visible spectrum. Schofield and Dutton (123) used visible absorption in their studies of the sources of color in soybean lecithin. Pons *et al.* (124) demonstrated by visual spectroscopic methods how the different modified forms of gossypol in extracted crude oils affect the determination of this pigment. Studies of the visible absorption curves revealed the causes for errors attending the determination of gossypol, especially after reaction with aniline reagent. Boatner *et al.* (125) made much use of visible absorption spectra to investigate various pigments, other than gossypol, in cottonseed.

Holman *et al.* (126) and Holman and Burr (127) demonstrated that the so-called "alcoholic-alkali color" of rancid fats is probably not due to the formation of *p*-quinones from α -dicarbonyl compounds arising during oxidation of fat or to any extent, to chroman-5,6-quinone derived from tocopherol or its degradation products in alkali. The alcoholic-alkali color probably arises in part from compounds derived from the unsaturated fatty acids which are closely related to the compounds obtained from chroman-5,6-quinone by treatment with alkali, and it may result largely from other unsaturated carbonyl compounds which are oxidation products of unsaturated fatty acids. This conclusion, from spectrophotometric studies, should be compared to those of Golumbic (128) who, on the basis of chemical studies, assigned the darkening of vegetable oils undergoing oxidation to the formation of compounds related to the tocopherols.

O'Connor *et al.* (114,115) investigated the spectral properties of several vegetable oils in the visible region and related each observed absorption band to the pigments which gave rise to it. They also investigated the

effect of the processes of extraction (hydraulic pressing, continuous pressing, solvent extraction) and the effect of processing (alkali refining, bleaching, deodorizing) of the derived crude oils on the pigments as revealed by their absorption spectra in the visible region.

Ramarkrishnan (129) reported that butyl oleate can be determined by direct spectrophotometric measurements of its absorption at 400 to 405 m μ .

Another application of absorption in the visible region of the electromagnetic spectrum is the determination of color of oils. The American Oil Chemists' Society has fostered work on methods for estimating color as a means of grading of oils for over 35 years. For the present status of this work the reader should refer to the current reports of the Color Committee of this society (130). Stillman (131) published a condensed review of this subject in 1955.

Two methods for measuring color have been recommended by the Color Committees and have been adopted by the American Oil Chemists' Society, namely, the Wesson method, which involves visual comparison of the color of a tube of oil with standardized color (Lovibond) glasses (132), and a photometric method (133) designed to give values, measured with a wide band spectrophotometer, that are supposedly identical with those obtained by the color comparison method.

It should not be amiss to digress at this point to indicate, for the benefit of those readers who may not be entirely familiar with the inherent difficulties involved in the measurement of visual color, the basic nature of this problem. The difficulty of providing an adequate method for the evaluation of the color of an oil has been said to be caused by lack of understanding of what is meant by the word "color." The problem is moreover further complicated by a lack of understanding of the reason why it is desirable to evaluate color by some practical method that is comparative and reproducible.

If color is to be measured merely to satisfy consumer preference of the end product, then visual color-matching is adequate. For example, a shirt collar is snowy white whether or not a yellow tint is masked by an old-fashioned bluing or by the more modern optical bleach. The collar is white simply because it appears white and appearance is the only factor involved. But the measurement of color in an oil, even after alkali-refining, is not done merely to control its appearance. Stillman (131) has stated with reference to the purpose for the measurement of the color of oils: "Color and bleach methods are those (methods which are) used to determine the amount of color in an oil, how easy it is and how much it costs to remove that color, and how much color remains in

the oil after bleaching." The problem therefore involves much more than merely the visual appearance of the alkali-refined oil.

If one considers two oils, each of which contains an equal amount of a red color (pigment), but one of which contains in addition about an equal amount of a green color (pigment), the green pigment in the second oil will mask the red color in the same manner as the bluing masked the yellow in the example of the snow-white collar mentioned above. The second oil will be visually much lighter in color than the first oil, but the difficulties and the cost of removing the two pigments from the second oil may be considerably greater than to remove only the red color of the first oil. The problem of evaluating the color of an oil is, therefore, not merely one of evaluating the visual appearance of an alkali-refined oil, but one of measuring the kind and quantity of pigments which the oil contains. If one substitutes in Stillman's statement quoted above, the word "pigment" in place of "color," the nature of the problem, but not necessarily its solution, becomes clearer; it is to identify each pigment or absorbing compound in the oil and to devise a method for its quantitative determination. Jefferson (134) described the problem in a similar manner and discussed simplified methods by which a solution might be attained.

The present approach to the problem of oil color is progressing toward the direct spectrophotometric determination of the pigments or of the intensities of an absorption band characteristic of each pigment. In either case, visible absorption spectrophotometry appears to be destined to play an increasingly important role in this field.

In 1957, Pohle and Tierney (134a) described a spectrophotometric method for the evaluation of color in vegetable oils which has the advantages of expressing the amount of color, i.e., pigment, more exactly, provides a more accurate measure of the reduction of color during bleaching and a more exact evaluation of the comparative efficiencies of bleaching earths with respect to the removal of oil-soluble color bodies.

Complete color designations (C.I.E.) were obtained by Melvin *et al.* (134b) for about 200 samples of commercial vegetable oils. They found that in only a very few cases was there agreement between tristimulus values (complete color designations) and Lovibond values of the oils. A particularly wide disagreement was found in the respective values in the case of soybean and cottonseed oils.

Another application of visible absorption is the measurement of color produced by certain specific chemical reactions. The determination of vitamins involves color reactions to which spectrophotometric methods

have been applied, e.g., the Carr-Price (135) method for vitamin A which involves the production of a blue color by reaction of the vitamin with antimony trichloride followed by the spectrophotometric measurement of the developed color. Many modifications of this procedure, which is described in detail in *Methods of Vitamin Assay* (93) of the Association of Vitamin Chemists, have been suggested. The reader is referred, particularly, to those of Winton and Winton (136) and of Dann and Evelyn (137). A very specific application of this method is that of Moor (138) who applied the method to the determination of vitamin A in milk.

α -Tocopherol (vitamin E) is also determined by means of visible absorption, by the Emmerie-Engel (139), or the more generally applied modification of Parker and McFarlane (140) or Quaife and Biehler (141). This method involves the development of a red color with ferric chloride and 2,2'-dipyridyl. It can be used only for the determination of α -tocopherol (vitamin E) as described in a modification by Deacon and Wamble (142), but it can be applied for the determination of total tocopherols by the modification of Edisbury *et al.* (143).

Ascorbic acid (vitamin C) is also determined by spectrophotometric measurements in the visible region after reaction with 2,6-dichlorophenol-indophenol reagent to produce a colored reaction product as described in the methods of Bessey (144) and Hochberg *et al.* (145).

The most commonly used methods for the determination of gossypol in cottonseed and cottonseed oil involve measurements in the visible spectrum of the color developed by reaction with *p*-anisidine (124,147), antimony chloride (146), or aniline (146a).

Methods involving the development and measurement of color in the visible region of the spectrum have been used for estimating degree of oxidation and oxidative rancidity in fat products. Among these is the thioburbituric acid method, which depends on the development of a red-colored complex between thioburbituric acid and a product of oxidation, followed by spectrophotometric measurement of the developed color at 530 m μ . Other applications include the measurement of oxidation in dried milk products, described by Sidwell *et al.* (148); the determination (149) of fatty acid oxidation produced by ultraviolet irradiation; adaptation of the method of Dunkley and Jennings (150) for measuring rancidity in milk; and the determination of oxidative rancidity in frozen herring by Fridriksdotter (151). Dische *et al.* (152) described a color reagent, comprised of α -methylindole and hydrochloric acid, for the

determination of α -keto acids and α -keto- and hydroxyaldehydes. Taylor and Smith (153) employed 1,2-diamino-4-nitrobenzene for the detection and determination of α -keto acids in blood and urine.

2,4-Dinitrophenylhydrazine has been used for the determination of oxidation products. Buss and Mackinney (154) determined the carbonyl compounds in rancid corn oil by means of the 2,4-dinitrophenylhydrazones and demonstrated that two of the products of oxidation were *n*-undecanal and *n*-undecenal. Mendelowitz and Riley (155) used the same reagent for the determination of long-chain fatty acids containing ketonic groups. They showed that licanic acid, which contains a keto group, can be determined in the presence of eleostearic acid by means of this reagent. The volatile carbonyl compounds, resulting from decomposition of peroxides of methyl esters and highly unsaturated acids, were identified by their dinitrophenylhydrazones by Toyama and Suzuki (156). They were able to identify crotonaldehyde, *n*-butylaldehyde, 2-pentenal, and *n*-hexanal among the products of decomposition of the peroxides of sardine oil by means of this reagent.

Measurements of absorption spectra in the visible region have also been used to determine phosphorus (157) in lipids after conversion of the phosphorus to a phosphoric-molybdic acid complex and reducing the complex to molybdenum blue; and copper (158) in oils and fats after development of a colored derivative of dibenzylthiocarbamic acid. Stewart (159) used chromatotropic acid for the determination of glycerides in lipid extracts, and Duewell (160) applied the Lederer and Kiun (161) colorimetric method (acetic anhydride and concentrated sulfuric acid) for the simultaneous determination of cholesterol and the triterpenols in the unsaponified fraction of wool wax.

The foregoing examples are representative of many other applications of visual spectroscopy which have been used successfully to solve problems in the fatty acid field.

(c) Raman Effect

When radiation strikes a given medium, most of it will either be transmitted through or be absorbed by it, but a small portion will be reflected or scattered as it strikes the medium. Examination of this scattered radiation reveals that it consists of three types known as *Tyndall scattering*, *Rayleigh scattering*, and *Raman effect*. The Raman effect differs from either Tyndall or Rayleigh scattering mainly by the fact that, although there is no change in frequency of either Tyndall or Rayleigh

scattering, the radiation from Raman effect consists of a series of frequencies which differ from the incident radiation. Consequently, if monochromatic radiation is examined spectrographically, it is found that after scattering it is no longer monochromatic but instead is composed of the original frequency from Tyndall and Rayleigh scattering and new frequencies from Raman effect (Fig. 21). If the recorded new frequencies are higher than the incident radiation, they are called anti-Stokes lines; if lower, Stokes lines. Stokes lines are, generally, considerably more intense and only they have practical importance in chemical spectroscopy.

The difference between the frequency of a Stokes or anti-Stokes line and the incident radiation is called the Raman frequency. It should be noted that a Raman frequency does not denote a position in the electromagnetic spectrum but a frequency difference between incident and scattered lines. These distances are sometimes referred to as Raman shifts. Both Stokes and anti-Stokes lines for the carbon tetrachloride molecule excited by the strong lines of mercury at 4358 and 4047 Å. are shown in Figure 21. It

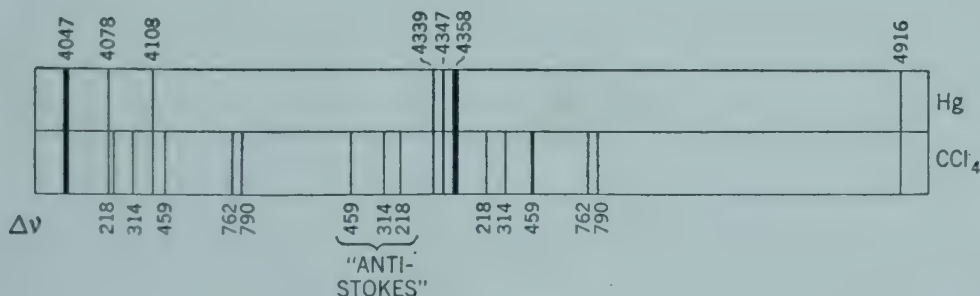


Fig. 21. Raman spectra (161a).

should be noted also that Raman frequencies of a given substance are independent of the incident radiation, e.g., in Figure 21 they are the same for incident radiation Hg 4358 Å. and for Hg 4047 Å.

Radiation in the visible region of the spectrum is commonly used as the source of excitation in producing the Raman effect because the higher energy of ultraviolet radiation may destroy some types of materials. Monochromatic lines from the mercury vapor lamp are most commonly employed. However, isolated lines from the iron arc spectrum in the ultraviolet are also used, particularly where higher intensities are required. Because visible radiation is commonly employed as the source of excitation, Raman effect is discussed here as part of the visible portion of the

electromagnetic spectrum, although, for convenience, it is indicated in Figure 21 as lying in the ultraviolet region. Actually, both the incident and Raman lines may be in either region and the use of an ultraviolet or visible exciting source does not affect the principles or applications discussed.

In the Raman effect, part of the energy of the incident photon is used to excite a vibration, and the remainder escapes as a photon of energy lower by the amount taken up by the molecule. The difference in energy between the incident and scattered photon is the energy taken up by the molecule in undergoing a characteristic transition of vibrational-rotational energy level. This difference in energy is related to the observed difference in frequency by the quantum equation $\Delta E = h\nu$. Thus, the principle factor of interest is the difference in frequency between that of the scattered spectral line (Raman line) and that of the exciting or incident radiation. This is the Raman frequency and it is also a measure of the frequency of the vibrational-rotational transition within the molecule. The differences in frequency between the incident radiation and the scattered lines are thus intimately connected with the energy states of the molecule. These energy differences relate to the vibrational and rotational energy levels.

Infrared absorption spectra are also associated, as will be seen later, with the absorption of radiation to produce transitions in the vibrational and rotational energy levels within the molecule. Infrared absorption occurs only when there is a change in the electric moment of the molecule, and Raman effect only when there is a change in the polarizability. Thus, antisymmetrical vibrations usually give rise to strong infrared absorption bands while symmetrical vibrations result in a strong Raman effect. Hence, infrared absorption spectra and the Raman effect give the same kind of molecular information and can therefore either supplement or complement one another.

Raman lines, excited by unpolarized light, may be more or less polarized and Raman lines, excited by polarized light, may be depolarized. The state of polarization of a Raman line is described in a precise fashion by its depolarization factor, i.e., by the ratio of the intensities of the line, measured when the polarizing device is oriented so that the polarizing direction is, respectively, perpendicular and parallel or,

$$\rho_n = I_s/I_P$$

where, ρ_n is the depolarization factor when the incident radiation is natural or unpolarized light, and I_s and I_P are the two intensities perpen-

dicular (S from the German *senkrecht* = perpendicular) and parallel, respectively. ρ_n takes values from 0 to $6/7$.

The fact that the polarization of a Raman line is related to the symmetry of the molecular vibration from which the line originates is of importance in the interpretation of Raman spectra. In the elucidation of molecular structure from Raman and infrared spectra, the number of lines for which ρ_n equals $6/7$ and the number for which ρ_n is less than $6/7$ is the basis on which many possible structures may be eliminated from consideration (4). Use of Raman effect for purposes of chemical spectroscopy consists, therefore, of evaluating the Raman frequencies, and the intensities and state of polarization of the Raman lines. Harrison (4) has shown in detail how infrared and Raman effect together can constitute one of the most important tools for the determination of molecular structure.

Raman data has proved valuable in the identification of certain linkages in organic compounds, in determinations of structure, and in differentiation between proposed structures. Several examples may be cited to indicate the importance that the Raman effect may have in fatty acid chemistry. Hende (162) suggested the use of Raman frequencies to identify and estimate quantitatively the individual fatty acids in natural fats and oils. Claims have been made that the saturated acids up to C_{11} can be identified by characteristic Raman frequencies. Menzies (163) has discussed the status and applications of Raman spectroscopy in Great Britain. Raman spectra of a few normal straight-chain fatty acids were reported by Kohlrausch and co-workers (164, 165). They included members of the homologous series from formic (HCOOH) through caproic ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$) acid and the corresponding methyl and ethyl esters, methyl ketones, and acid anhydrides and chlorides.

Differentiation between *cis*- and *trans*-isomers has been one of the principal achievements of Raman spectroscopy. Studies of the ethylenic bond in fatty acids have established a frequency shift of about 1650 cm.^{-1} for the *cis*-acids (oleic, ricinoleic, linoleic, etc.) and about 1670 cm.^{-1} for the corresponding *trans*-forms (elaidic, ricinelaidic, linolelaidic, etc.) (166, 167). The potential importance of this generalization in fatty acid chemistry is obvious.

It has been found that the shifts characteristic of the carbonyl group of formaldehyde, HCHO , disappear when this aldehyde is added to water and in solution the Raman spectrum becomes similar to that of glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$. Paraldehyde and paraformaldehyde do not exhibit carbonyl shifts in keeping with their cyclic structures. In equilibrium mixtures of a tautomeric substance, such as acetoacetic ester, both

methylene and carbonyl shifts are observed. The Raman frequencies of the C=O group in various fatty acids, aldehydes, esters, ketones, etc., are sufficiently different to permit their identification, as may be seen from Table 60, in which there are listed the characteristic Raman frequencies of principal interest to the fatty acid chemist.

The Raman shift exhibited by oximes derives from the presence in these compounds of the characteristic C=N linkage and provides definite evidence of the structure of such derivatives. It has been established from measurements of the Raman effect of nitriles and isonitriles, that compounds containing the C≡N linkage have a Raman frequency about 2150 cm.⁻¹ (Table 60).

TABLE 60
Characteristic Raman Frequencies

Group	Frequency, cm. ⁻¹	Group	Frequency, cm. ⁻¹
O—H	3400	C=C	1620-1670
C—H (aromatic)	3050	C—C (aromatic)	1580-1620
C—H (aliphatic)	2920-2970	N=O (nitro)	1565
S—H	2570	C—C	1190
			
C≡C	2100-2250	N—O	1000-1080
C≡N	2150	C—F	1050
C=O (anhydrides)	1750	C—C (aliphatic)	990
C=O (aldehydes)	1720	C—N (nitro)	910-930
C=O (ester)	1720	C—N (amine)	880
C=O (ketone)	1710	C—O (alcohol)	820-880
C=O (acid)	1650	C—Cl	650-710
C=N	1650	C—S	645
N=O (nitrate)	1640	C—Br	570-600
N=O (nitrite)	1640	C—I	500-530

Evidence for the presence of a carbon-carbon triple bond in some animal fats, and for the presence of a terminal double bond in certain aliphatic C₁₀-acids have been obtained (167) from Raman frequency measurements. Hydroxyl frequencies, hydrogen bonding, and dimer formation have been investigated with the aid of the Raman effect (168,169). Yvernault (167) discussed applications and value of the Raman effect in fatty acid chemistry, and pointed out certain advantages in measurements of this type over those of infrared absorption.

The potentialities of Raman effect as a useful tool in fatty acid chemistry was definitely established in the early 1940's but it was not ex-

tensively employed probably because at the time, only photographic instruments were available and these required specialized skill to operate and considerable time to obtain characteristic Raman frequencies. This position is exactly analogous to that obtaining with infrared absorption spectra about the same period. Subsequently, direct reading instruments which permit measurement of Raman frequencies with considerable simplicity and speed became available, but still only a very few applications in the field of fatty acids and related compounds have been reported, principally in the Russian literature (170). Thus, while infrared absorption has become an almost indispensable tool for investigations of fatty acids and related compounds, for reasons which are not readily apparent, the Raman effect has been almost neglected despite its considerable promise.

(d) Fluorescence and Reflectance

Two other uses of radiation in the visible portion of the electromagnetic spectrum should be mentioned because of their applications to fat products. These are fluorescence and reflectance.

Fluorescence. Usually a substance absorbs, transmits, or reflects radiation without altering its frequency. If radiation is absorbed, causing a change in energy level in accordance with the quantum law, this absorption may be dissipated in the form of heat, as in the usual absorption process, or it may be remitted by a return of the excited electron to its original energy level. This latter process is emission and, obviously, will occur at the same frequency as the incident radiation. Under certain conditions, the absorbed energy represented by the electron in the excited state may be remitted in part by a return of the excited electron to a less excited state, but one which is more excited than the original state before absorption of the incident radiation. In other words, only part of the absorbed energy is re-emitted and the frequency of the re-emitted radiation must, in accordance with the quantum law, be less than that of the incident radiation (Stoke's law). If this type of partial re-emission is immediate, the process is fluorescence; if it occurs over an interval of time, it is called phosphorescence.

The color of fluorescence excited by ultraviolet radiation has been suggested as an aid in the identification of fats and oils. For this purpose the fluorescent colors of several fatty acids have been compiled. For some of the more common acids these are: formic, pale lilac; acetic, colorless; propionic, colorless; butyric, weak yellow; caproic, red violet; lauric,

vivid violet; palmitic, pale yellow-grey; stearic, white with a violet tinge; oleic, strong violet; erucic, vivid violet; and lactic, pale lilac. No particularly useful application seems to have been made of this property. The colors of the fluorescence of natural oils depend upon that of the acids which they contain and these have been used for the detection of adulterants or contaminants.

Fluorescent colors have frequently been reported in the literature for natural oils, as indicated by the compilation in Table 61. In general, these

TABLE 61
Fluorescent Colors of Fats

Fat	Color	Fat	Color
Cacao butter	Bright white	Lard	Very pale blue
Synthetic fats	Grayish-white	Hazelnut	Light blue
Linseed	Milky yellow	Castor	Blue
Sunflower	Light yellow	Corn (maize)	Yellowish-green
Walnuts, sesame, almond, olive	Yellow	Pine	Light green
Rapeseed	Brownish-yellow	Soybean	Dark green

colors have little practical significance because they depend to an appreciable extent on the type of process used to extract the oil from the respective raw material, the nature of the process used and thoroughness of refining, the age of the oil, and particularly the extent of autoxidation, etc. Haitinger *et al.* (171) reported that butter has a yellow fluorescence, and that margarine (presumably uncolored) and synthetic fats appear grayish-white.

Cortese (172) examined the fluorescence of various olive oils and found that the yellow fluorescence of the raw oil could not be distinguished from the blue fluorescence of the refined oil as fluorescence of the chlorophyll and carotene interferes. The use of synthetic food colors or carotene in present day margarines vitiates the value of fluorescent colors for purposes of identifying these products.

Dutton and Edwards (173) correlated the fluorescence of egg lipids with browning and Scholfield and Dutton (173a) described the use of fluorescence as a measure of brown substances in soybean lecithin. Grant and Lips (173b) showed that the fluorescence of lard disappears as rancid odors develop, indicating that fluorescence of lard is linked to the presence of natural antioxidant substances which are altered by oxidation. Bryant

and Biggs (173c) describe the detection of vegetable fats in butterfat by means of fluorescence. Cortese (172), however, was able to simulate the fluorescence of a pressed oil by adding carotene or chlorophyll to a refined oil, and the fluorescence characteristic of lard has been shown to be due to substances absorbed from infusorial earth used as a bleaching agent (173d).

Fluorescence is characteristic of most fats and oils, but it is very variable and depends on many factors besides glyceride composition. At times it may have some use in indicating adulteration or contamination, but it cannot be relied on for identification of a specific fat or for detecting a specific impurity. Sims and Cooper (174) investigated the fluorescence of drying oils and the effect of heating on this fluorescence. They concluded that the nonglyceride and glyceride components of the oil contribute to the observed fluorescence.

Fluorescence phenomenon of olive oil has been the subject of numerous investigations, including those of Lunde and Stiebel (174a) who examined more than 300 samples, and those of Stratta and Mangini (174b), Glantz (174c), and Lunde *et al.* (174d). Other investigations of the fluorescence of vegetable oils include those of Marcelet and Debono (174e), Guillot (174f), and Wagner (174g). Lewkowitsch (174h) reported similar studies on animal oils.

Reflectance Spectrophotometry. Another use of radiation in the visible portion of the electromagnetic spectrum is that of measuring the color of opaque materials by reflectance spectrophotometry. The color of an opaque object arises from that portion of the radiation falling upon the object which is reflected by it back to the eye of the observer. By means of a reflectance spectrophotometer, or more usually a reflectance attachment on an absorption spectrophotometer, the reflectance may be measured and automatically recorded as a function of the wavelength throughout the visible portion of the spectrum. From a reflectance curve and a precisely defined system, the C.I.E. (175) tristimulus values, trichromatic coordinates, and psychophysical attributes of color can be calculated and Munsell renotations computed. Morris *et al.* (175a), in an article on the determination of the color of peanut products, have described each step required to obtain reflectance curves, C.I.E. data, and Munsell renotations.

Bacon and Smith (176) have described the application of spectral reflectance for the direct measurement of the relative efficiency of detergents. Spectral reflectance measurements have been used to evaluate the color of many opaque objects, including that of many food products.

The importance of reflectance phenomena in the field of fat products was recognized by the American Oil Chemists' Society when the name of its long-standing Oil Color Committee was changed (130) in 1955 to the Color Committee and two subcommittees were established, one for the measurement of oil color (by transmittance) and the other for the measurement of surface colors, soaps, detergents, etc., by means of reflectance measurements.

5. Infrared

(a) Introduction

Infrared radiation was discovered by Herschel in 1800 but it was not applied for analytical purposes until 1892 by Julius. In 1905 Coblentz published the first so-called "library" of infrared spectra. The first technical article devoted exclusively to applications of infrared spectroscopy to fatty acid products was published by Gibson in 1920, but little subsequent use was made of this phenomenon in the field of fat chemistry during the following two decades. Even in the following decade (1940-49) only 23 publications appeared which dealt with applications of infrared spectroscopy to fatty acids, but between 1950 and 1956 more than 140 such articles appeared and the number has continued to increase since then. Today infrared spectroscopy is an indispensable tool in fatty acid research and even in many control laboratories (177).

Following the discovery of infrared radiation by Herschel in 1800, investigations of this new radiation were at first devoted exclusively to experiments with infrared atomic absorption. It was not until 1918 that the work of Sleator (178) introduced a new approach to problems of molecular structure by means of infrared spectra. Thereafter emphasis was placed almost exclusively on molecular absorption and investigations in the atomic field have only recently been resumed (179). Use of the infrared region of the electromagnetic spectrum for chemical analysis has been confined almost exclusively to molecular absorption, and this type only will be considered here.

The laws of emission and absorption of infrared radiation are similar to those in the ultraviolet and visible regions of the spectrum and the fundamental equation,

$$\Delta E = h\nu$$

is valid for all transmission and absorption processes. The wavelengths of infrared radiation are greater than those of ultraviolet; hence, in

accordance with the foregoing equation, the energy changes are correspondingly smaller, of the order of magnitude of one kilocalorie per mole. Energy changes of this magnitude are insufficient to produce transitions between electronic orbits.

Infrared molecular absorption spectroscopy is based upon changes within the molecule between different vibrational levels within a single electronic level. These vibrational changes do not occur without accompanying changes in rotational levels, and infrared absorption spectra, therefore, appear as bands consisting of many lines so close together in wavelength that they can be resolved only with special instruments of very high resolving power. These spectra are thus vibrational (or strictly vibrational-rotational) band spectra involving energy level changes less than those of ultraviolet or x-ray (electronic) spectra and are greater than those of the pure rotational spectra of the microwave region.

Fundamental studies have established for some simple molecules the entire pattern of vibrational-rotational energy level transitions to account for all of the observed lines in highly resolved spectra. Such studies, however, have not been particularly successful in dealing with more complicated molecules and applications of infrared spectroscopy to chemical analysis have been based on a more empirical approach.

Julius (180) was one of the first to suggest an empirical use of infrared

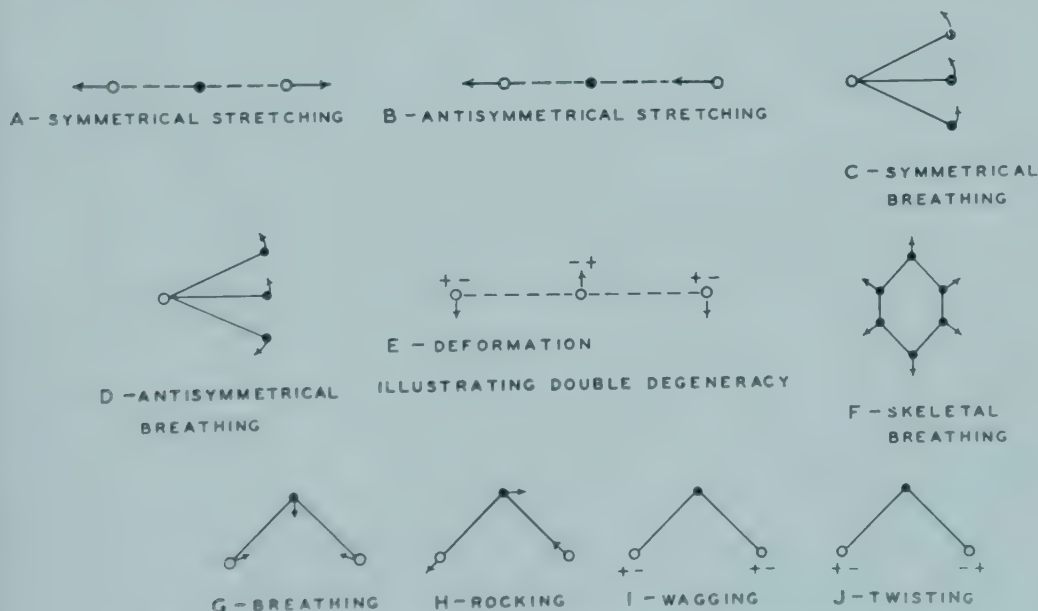


Fig. 22 Modes of vibration which give rise to infrared absorption bands.

absorption data for the purposes of chemical analysis. He showed that the infrared spectra of all compounds containing a specific group exhibited the same absorption maxima, i.e., the infrared spectra of compounds containing the methyl group always exhibit a band with maximum at $3.45\ \mu$. Such empirical correlations of vibrating groups with specifically observed absorption maxima suggested to Julius the possibility of chemical identifications, a means of obtaining preliminary evidence for or final confirmation of molecular structure, and by a consideration of the intensities of the respective bands, a method for quantitative chemical analysis. These empirical correlations are today the basis for most analytical applications of infrared absorption spectra. The various types of group vibrations with names commonly applied to each of them are shown in Figure 22.

(b) *Empirical Correlations*

Most applications of infrared absorption spectroscopy are for purposes of analysis and hence are based on correlations established between observed absorption bands and vibrating groups which give rise to them. Before infrared spectroscopy can be applied in a specific field some investigations are required to establish essential correlations. Reference is therefore made below to several general survey articles relating to application of infrared spectra to fatty acids, their derivatives, and related materials. Although somewhat preliminary in character, they are very important because they provide data needed for use of these spectra in the analysis of fats and oils.

Coblentz (181), Gibson (182), and Barnes *et al.* (183) established several correlations between observed absorption bands and vibrating groups which give rise to them. Gamble and Barnett (184) established several correlations having application to drying oil chemistry. However, it was not until 1950 that Shreve *et al.* (185) published infrared spectra for several long-chain fatty acids, esters, and alcohols dissolved in carbon disulfide, and accompanied them with several band correlations. O'Connor *et al.* (186) published quantitative spectra for several fatty acids and their methyl and ethyl esters in chloroform solution, together with absorptivities at significant wavelengths, thus making possible relative quantitative comparisons for these substances.

Sinclair *et al.* (187) reported the spectra of saturated fatty acids and esters, and Sinclair *et al.* (188) described the spectra of unsaturated fatty acids and esters. The latter authors made several correlations between observed bands and vibrating groups and compared the spectra of solutions with those of solid films or mulls.

In the spectra of solutions of unsaturated fatty acids, the intensity of the band at $3.3\ \mu$, attributed to a C—H stretching vibration of the C=C—H group, was shown to increase with increasing degree of unsaturation, while the intensity of the bands at 3.43 and $3.51\ \mu$, arising from —CH_2 stretching vibrations, decreased in the same series. These intensity measurements require the use of an instrument capable of high resolution at these wavelengths. The intensity of a band at $13.0\ \mu$ in the spectra of saturated fatty acids and esters, attributed to a CH_2 rocking vibration, was shown to increase progressively with chain length. This may be significant in estimations of chain lengths of unknown saturated fatty acids.

The spectra of crystalline acids (films or mulls) show much more structure. The C=O stretching vibration occurs at 5.88 to $5.89\ \mu$ in the spectra of the even-number carbon acids, but it occurs at $5.87\ \mu$ in the spectra of the odd-number acids, thereby providing a means for distinguishing between carbon chains containing odd and even numbers of carbon atoms. A progression of bands, spaced at fairly even intervals of $0.05\ \mu$, appear in the spectra of the solid forms between 7.4 and $8.5\ \mu$, while spectra of solutions exhibit only broad diffuse bands.

Sobotka and Stynler (189) reported on the infrared spectra of isoacids with a branching methyl group on the second carbon atom from the end of the chain, anteiso acids with a branching methyl group on the third carbon atom from the end of the chain, and neoiso acids with two branching methyl groups on the second to last carbon. Iso acids can be distinguished by a splitting of the $7.25\ \mu$ band into two components of about equal intensity, "isopropyl splitting." Neo acids exhibit the same splitting of the $7.25\ \mu$ band, but the longer wavelength component is the more intense, "tert-butyl splitting." Anteiso acids show no splitting, but the $7.25\ \mu$ band is much stronger than in the spectra of normal acids.

Branched, long-chain fatty acids have been studied by Freeman (190) who reported spectral data for 27 of these compounds and attempted to correlate features of their infrared spectra with types of chain-branching. He considered position of branching and the number and length of the branching side chains. Branching on the α -carbon, or near the carboxyl group, can be detected by observation of the bands at 7.78 and $8.00\ \mu$. In straight-chain compounds the band at $7.78\ \mu$ is the more intense of this pair. Substitution on the α -carbon reverses this relation. Substitution within five carbons of the carboxyl group can be recognized by shifts in wavelength positions of the band at $8.00\ \mu$. The lengths of the substitute branches are indicated for the ethyl group by a band at $12.95\ \mu$, for the

n-propyl group by a band at $13.5\ \mu$, and for the isopropyl and *tert*-butyl by splitting of the band at about $7.25\ \mu$ into two components. The number of branches can be detected by determination of terminal methyl groups. From a study of the infrared spectra of castor oil, Narayan and Kulkarni (191) have shown that the C—OH stretching band at $2.9\ \mu$ can be used to detect and possibly to determine this oil.

O'Connor *et al.* (192) discussed the infrared absorption spectra of molecular compounds of acetamide and long-chain fatty acids.

The spectra of aluminum soaps of fatty acids from C_6 to C_{18} have been investigated by Harple *et al.* (193) and compared with the spectra of the fatty acids. The spectra of aluminum monoacid soap, $Al(OH)_2(RCOO)$, and aluminum diacid soaps, $Al(OH)(RCOO)_2$, differ from the triacid soaps in not exhibiting a "fatty acid" band at $5.82\ \mu$ (C=O stretching of COOH group). These results were interpreted to indicate that aluminum triacid soaps do not exist as chemical compounds, i.e., as $Al(RCOO)_3$, but as mixtures or loose compounds of the diacid soap and fatty acid, an interpretation consistent with the fact that the triacid soaps contain fatty acids extractable with cold isooctane in contrast with the aluminum mono- and diacid soaps which contain almost no extractable acid. Aluminum monoacid soaps can be distinguished from diacid soaps by their infrared spectra as they exhibit a broad band at $3.0\ \mu$, indicating bonded O—H O groups, while the spectra of aluminum diacid soaps show a band at $2.7\ \mu$, indicating unbonded O—H groups. The spectra of soaps having compositions between the mono- and di-types exhibit bands both at 2.7 and $3.0\ \mu$, indicating that the monoacid and diacid soaps exist as discrete compounds.

Barcelo and Bellanato (194) reported infrared spectra for several vegetable oils and, for comparison, the spectra of long-chain fatty acids and glycerides over the entire range of the sodium chloride and potassium bromide salt crystal regions, i.e., 2.5 to $28.0\ \mu$. Absorption maxima exhibited by the oils, but not by the fatty acids, were observed at about 9.13 , 8.97 , 8.77 , and $7.87\ \mu$. The infrared spectra of aliphatic acids, their esters, and some vegetable oils were also reported by Batishcheva and Mironova (195) who discuss, in particular, quantitative applications of these spectra. Both of these groups of workers tabulated correlations between observed bands and vibrating groups. Kuhrt and co-workers (196) described the infrared spectra of monoglycerides; and O'Connor *et al.* (196a) compared the spectra of mono-, di-, and triglycerides, and pointed out their potential quantitative applications. Shreve and co-workers published surveys of the infrared spectra of epoxidized (197) and

peroxidized acids (197a), emphasizing those absorption bands of importance in the recognition and measurement of these derivatives. O'Connor *et al.* (198) discussed the infrared spectra of hydroxy acids.

Baer (199) and Baer *et al.* (199a) published the infrared spectra of L- α -lecithins, including tabulations of the positions of wavelength maxima, relative intensities, and probable assignments for several of the more prominent bands. Freeman (200) presented spectra for various lipoproteins. The spectra of pentaerythritol esters of fatty acids have been discussed by Nicholls and Hoffman (201). Davison and Christie (201a) described the infrared spectra of 24 semicarbazones of ketones and aldehydes and their use in the identification of these compounds. Other surveys of infrared spectra have been published by Guertin *et al.* (201b).

The data compiled from the above-mentioned literature, combined with correlations obtained in other investigations involving in each case only one or two infrared absorption bands, have led to the establishment of relationships between observed spectra and characteristic groups in fatty acid molecules upon which many applications can be based. The increase in the number of publications on the application of infrared absorption spectra to fatty acid chemistry during the past decade has been brought about by two factors, namely, (1) the availability of commercial instruments which can be readily used by chemists in analytical laboratories, and (2) the increasing number of published correlations which suggest an increasing number of potential applications. O'Connor (177) compiled a list of 100 absorption bands employed in the application of infrared spectroscopy to fatty acid chemistry, which is reproduced in Table 62.

TABLE 62

Infrared Absorption Bands Applicable to Fatty Acids and Related Products*

No.	Wavelength position of observed band, microns	Vibrating group giving rise to observed absorption band
I. O—H, C—H, N—H, C—D, P—OH, and P—H stretching vibrations. Regions 2 to 5 microns		
A. O—H stretching		
1	2.75–2.80	Free —O—H
2	2.82–2.90	Bonded —O—H...O of single-bridged dimer
3	2.95–3.25	Bonded $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{H} \dots \text{O} - \text{H} \dots \text{O} - \end{array}$ of double-bridged polymer or cyclic

(continued)

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
		$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{—O} \quad \text{O—dimer} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
		<i>B. C—H stretching</i>
4	3.00–3.05	$\text{R}\equiv\text{C—H}$
5	3.22–3.25	$\text{R}_2=\text{C—H}_2$
6	3.28–3.32	$\text{R}_2=\text{C—HR}$
7	3.40–3.45	R—C—H_3
8	3.42–3.50	$\text{R}_2\text{—C—H}_2$
9	3.45–3.48	$\text{R}_3\text{—CH}$
		$\begin{array}{c} \text{O} \\ \diagup \\ \text{R—C—H} \end{array}$
10	3.50–3.70	C—H and bonded O—H...O combination band
11	3.70	
		<i>C. N—H stretching</i>
12	2.85 and 2.95	Free N—H primary amide
13	3.00 and 3.15	Bonded N—H...primary amide
14	2.90–2.95	Free N—H secondary amide
15	3.00–3.05	Bonded N—H...secondary amide, single bridge (<i>trans</i>)
16	3.15–3.18	Bonded N—H...secondary amide, single bridge (<i>cis</i>)
17	3.22–3.25	Bonded N—H...secondary amide cyclic dimer
18	2.85 and 3.02	N—H primary amine
19	2.85–3.02	N—H secondary amine
20	2.95–3.12	N—H imines
21	3.20–3.30	N—H ₃ ⁺ amino acids
		<i>D. C—D stretching</i>
22	4.64	C—D
23	4.84	C—D
		<i>E. P—H, P—OH stretchings</i>
24	4.05–4.25	P—H
25	3.70–3.90	P—OH
		II. C=O and C=C, C≡C stretching vibrations. Region 3.0 to 6.0 microns
		<i>A. Aldehydes</i>
		$\begin{array}{c} \text{H} \\ \diagup \\ \text{RC=O, saturated} \end{array}$
		$\begin{array}{c} \text{H} \\ \diagup \\ \text{PhC=O, aryl} \end{array}$
		$\begin{array}{c} \text{H} \\ \diagup \\ \text{R—CH=CH—C=O, } \alpha, \beta \text{ unsaturated} \end{array}$

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
<i>B. Ketones</i>		
29	5.80-5.85	$\text{RCH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2\text{R}$, saturated
30	5.90-5.95	$\text{Ph}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$, aryl-alkyl
31	6.00-6.02	$\text{Ph}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{Ph}$, diaryl
32	6.00-6.05	$\text{R}-\text{CH}=\text{CH}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{R}$, α,β unsaturated
33	5.63	$\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$, 4-membered, saturated ring
34	5.73	$\begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$, 5-membered, saturated ring
35	5.81	$\begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \end{array}$, 6-membered, saturated ring, or
		$\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \end{array}$, 5-membered, α,β unsaturated ring
36	5.95	$\begin{array}{c} \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \end{array}$, 6- (or 7-) membered, α,β unsaturated ring
37	5.90-6.00	$\text{O}=\text{Ph}=\text{O}$, quinone, 2 $\text{C}=\text{O}$'s on 1 ring
38	6.05-6.10	$\text{O}=\text{Ph}-\text{Ph}=\text{O}$, quinone, 2 $\text{C}=\text{O}$'s on 2 rings
<i>C. Acids</i>		
39	5.68	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{OH}$, saturated monomer
40	5.80-5.88	$\begin{array}{c} \text{O} \quad \text{O} \\ \text{O} \dots \text{HO} \\ \text{R}-\overset{\text{ }}{\text{C}}-\text{OH} \dots \text{O}=\text{C}-\text{R} \end{array}$, saturated dimer

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
41	5.90-5.92	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{C}=\text{C}-\text{C}=\text{O}, \alpha, \beta \text{ unsaturated} \end{array}$
42	5.90-5.95	$\begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}=\text{O}, \text{ aryl} \end{array}$
43	6.00-6.05	Chelated hydroxy-acids, some dicarboxylic acids
<i>D. Esters</i>		
44	5.65	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{H}_2-\text{C}=\text{C}-\text{C}=\text{O}, \text{ vinyl ester} \end{array}$
45	5.75	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{R}-\text{C}=\text{O}, \text{ saturated} \end{array}$
46	5.80-5.82	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{R}-\text{C}=\text{C}-\text{C}=\text{O}, \alpha, \beta \text{ unsaturated, or } \text{R}-\text{COOPh}, \text{ aryl} \end{array}$
<i>E. Lactones</i>		
47	5.50	$\begin{array}{c} \text{CH}_2 \\ \quad \\ \text{R}-\text{CH} \quad \text{O}, \beta, \text{ or 4-membered saturated ring} \\ \\ \text{C} \\ \\ \text{O} \end{array}$
48	5.65	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{R}-\text{CH} \quad \text{O}, \gamma, \text{ or 5-membered saturated ring} \\ \\ \text{C} \\ \\ \text{O} \end{array}$
49	5.72	$\begin{array}{c} \text{CH}=\text{CH} \\ \quad \\ \text{R}-\text{CH} \quad \text{O}, \gamma, \text{ or 5 membered } \alpha, \beta \text{ unsaturated ring} \\ \\ \text{C} \\ \\ \text{O} \end{array}$
50	5.75	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{R}-\text{CH} \quad \text{O}, \epsilon, \text{ or 6-membered saturated ring} \\ \quad \\ \text{CH}_2-\text{C} \\ \\ \text{O} \end{array}$

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
51	6.0-6.1	F. C=C, C≡C stretching C=C <i>cis</i> only (weak when internal in symmetrical molecules)
52	3.03	HC≡CH
53	4.67-4.76	RC≡CH
54	4.44-4.58	RC≡CR
55	5.14 and 9.45	C=C=C
III. C—H deformations, saturated groups. Region 6 to 7 microns		
56	6.7-6.9	—C—H ₂ — group
57	6.8-7.0	—C—C—H ₃ group, asymmetrical deformation
58	7.15-7.20	—C—(C—H ₃) ₃ group
59	7.20-7.25	—C—(C—H ₃) ₂ group
60	7.25-7.30	C—C—H ₃ group symmetrical deformation
61	7.30-7.35	—C—(C—H ₃) ₂ group
62	7.45-7.50	—C—H— group
IV. C—O stretching and C—OH bending. Region 7.7 to 10.0 microns		
A. Alcohols		
63	7.2-8.6	Phenols
64	8.3-8.9	Tertiary open-chain saturated
65	8.9-9.2	Secondary open-chain saturated
66	9.2-9.5	Primary open-chain saturated
67	8.3-8.9	Highly symmetrically-branched secondary
68	8.9-9.2	α-Unsaturated or cyclic tertiary
69	9.1-9.2	Secondary with branching on one α-carbon
70	9.2-9.5	Secondary, α-unsaturated or alicyclic 5- or 6-membered ring
71	9.5-10.0	Secondary: di-unsaturated, α-branched and unsaturated, or 7- or 8-membered ring Primary: α-branched and/or unsaturated Tertiary: highly unsaturated
B. Acids		
72	7.75-7.80	C—O
73	8.40-8.45	C—O
C. Esters		
74	7.90-8.00	C—O
75	8.40-8.50	C—O
D. Ethers		
76	8.7-9.4	CH ₂ —O—CH ₂ , alkyl
77	7.8-8.1	Ph—O—Ph, aryl or =C—O, unsaturated
E. Anhydrides		

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
78	7.7-8.3	Cyclic
79	8.5-9.5	Open chain
80	6.90 and 10.0	F. Phosphorus P—O—Ph, aromatic
81	9.52	P—O—CH ₃ aliphatic
		V. C—H deformation about a C=C and skeletal and "breathing" vibrations. Region 10.0 to 15.0 microns.
		A. C—H bending
82	10.05-10.15	
83	10.20-10.36	<i>(trans only*)</i>
84	10.90-11.05	
85	11.17-11.30	
86	11.90-12.50	
87	13.0 > 15.0	<i>(cis only*)</i>

TABLE 62 (Continued)

No.	Wavelength position of observed absorption band, microns	Vibrating group giving rise to observed absorption band
* See text for table of wavelength positions of various combinations of conjugations involving these two internal groups.		
B. Skeletal and "breathing"		
88	9.75 and 11.55	Cyclopropane
89	10.9 and 11.3	Cyclobutane
90	10.31 and 11.16	Cyclopentane
91	9.63, 9.86, 11.05 and 11.60	Cyclohexane
92	11.2	Epoxy-oxirane ring derived from internal R—C=C—R (<i>trans</i> only)
93	12.0	Epoxy-oxirane ring derived from internal R—C=C—R (<i>cis</i> only)
94	11.8, 12.9, and 14.7	Benzene ring
95	12.0	Hydroperoxide
96	12.95	Ethyl
97	13.0	CH ₂ rocking on long carbon chain
98	13.5	n-Propyl
99	13.8	Hydroperoxide
100	7.5–8.5	Progression of bands in solid state spectra, probably due to wagging and/or bending mode of vibration of the C—H bonds of methylene groups. The number of bands in the progression is indicative of chain length.

* The exact position of maximum absorption depends upon whether the measurements were made on the pure liquid, solid, mull, or solvent and on the nature of the particular solvent. Several band positions are also critically dependent upon neighboring groups.

The value and range given in this table are from the author's collection of these bands in fatty acid materials mostly from original reports in technical journals. They represent average values of ranges of the various data that have been reported for the specific absorption.

(c) Application to Fat Products

An extensive number of reviews relating to actual and potential applications of infrared absorption spectroscopy to fatty acid chemistry have

appeared in several languages. Among these may be mentioned those of O'Connor (177,202,205), Ralston (203), Wheeler (204), Ahlers and O'Neill (206), and Binkerd and Harwood (207). The two last-mentioned reviews deal largely with the application of infrared spectra in the field of drying oils. Several shorter reviews covering specific applications of infrared spectroscopy to fatty acid chemistry have been published. Among the subjects covered are applications of infrared spectroscopy to paint research by Ahlers (208) and Hanson (209); to the coating industry by Brügel (210) and Lemon and Kirby (211); to surface compounds by Delsemme (212); to the graphic arts and waxes by Marron and Chambers (213); to additives in vegetable waxes by Marsel *et al.* (214); to waxes and polishes (215) and synthetic detergents (216) by Sadtler; and to cosmetics by P. A. Wilks (217). Reviews have also appeared in other languages, including those of Hasimoto (218) in Japanese, Volbert (219) in German, and Batischeva *et al.* (220) in Russian. Lecomte has contributed two reviews on the subject, one in German (221) and the other in French (222).

The reader may wish to supplement the brief discussion of infrared spectra given here by reference to one or more of the reviews mentioned above.

(d) *Determination of Trans-Configurations*

The first use of infrared spectra to distinguish between *cis*- and *trans*-bonds appears to have been made by McCutcheon *et al.* (166). They measured the spectra of several unsaturated acid esters from 5.0 to 6.5 μ and expressed the results as ratios of transmissions of the unsaturated compounds to that of ethyl stearate in order to avoid obscuring the weak absorption at 6.0 μ assigned to a C=C stretching by the strong carbonyl absorption in this region. They concluded from measurements of the corresponding ethyl esters that oleic acid has a *cis*-configuration, linoleic acid a *cis,cis*- and linolenic a *cis,cis,cis*- structure. Elaidic acid was shown to have a *trans*- and linolelaidic acid a *trans,trans*-configuration. These observations were confirmed by determining the Raman spectrum of each compound. The method has not proved very satisfactory because the C=C stretching vibration band at 6.0 μ is very weak and because there is interfering absorption from the strong C=O stretching vibration.

Rasmussen *et al.* (223) observed that a strong band at 10.3 μ in the spectra (Fig. 23) of unsaturated compounds appears to arise from a *trans*-C=C group. The band has since been shown to be due to a C—H

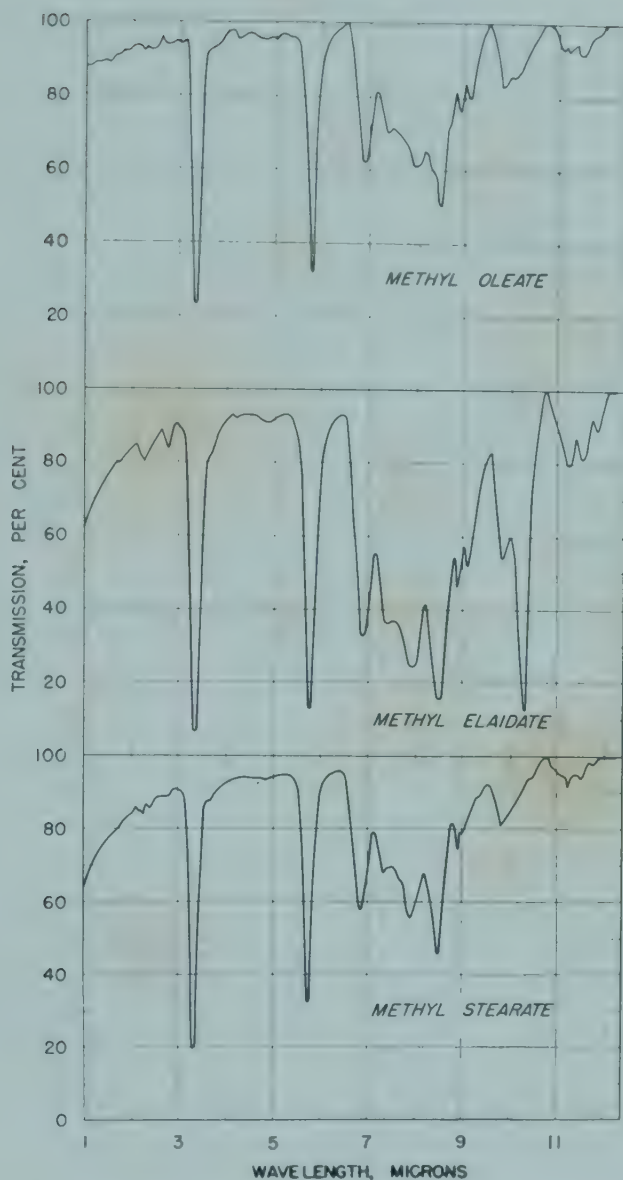


Fig. 23. Infrared absorption spectra of methyl oleate, elaidate, and stearate (258). Note strong absorption at $10.3\ \mu$ in spectrum of elaidate characteristic of *trans*-double bond.

deformation about a *trans*-C=C bond (224). Shreve *et al.* (225) developed a method for the determination of the concentration of isolated *trans*-bonds in a mixture of saturated and monounsaturated octadecenoic acids and related compounds based on quantitative measurements of this $10.3\ \mu$ band. The method was illustrated by the analysis of mixtures containing

oleic, elaidic, and saturated acids and of mixtures of the corresponding methyl esters and alcohols.

Shreve *et al.* also reported an absorptivity of about 0.4 for elaidic acid in carbon disulfide solution.

Paschke *et al.* (226) later showed that this absorptivity is about the same in the absorption spectra of pure methyl *cis*-9,*trans*-12-linoleate, and that the absorptivity of this band in the spectra of pure methyl *trans*-9,*trans*-12-linoleate is very nearly twice this value. These data strongly indicate that the absorptivities of the isolated *trans*-band at 10.3 μ are additive in nonconjugated compounds, and that the method of Shreve *et al.* can be extended to the analysis of polyunsaturated, nonconjugated olefinic acids and related compounds. Bickford *et al.* (32) found that the absorptivity at 10.3 μ in the spectra of α -eleostearic acid (*cis*-9,*trans*-11,*trans*-13-octadecatrienoic) is exactly twice that reported for elaidic acid, and in the spectra of β -eleostearic acid (*trans*-9,*trans*-11,*trans*-13-octadecatrienoic) it is three times that of elaidic acid. These data indicate that the intensities of the C—H deformation about the C=C group are additive in conjugated as well as nonconjugated compounds.

The use of the absorption band at about 10 μ in infrared spectra is not limited to the detection and determination of isolated *trans*-double bonds, although this is the only application which has been described in

TABLE 63
Wavelength Position of Absorption Band vs. Vibrating Group

No.	Wavelength (in μ) position absorption band	Vibrating group
1	10.05–10.15	$\begin{array}{c} \text{X} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$
2	10.20–10.36	$\begin{array}{c} \text{X} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{Y} \end{array} \quad (trans)$
3	10.90–11.05	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{X} \quad \quad \text{H} \end{array}$
4	11.17–11.30	$\begin{array}{c} \text{X} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Y} \quad \quad \text{H} \end{array}$
5	11.90–12.50	$\begin{array}{c} \text{X} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Y} \quad \quad \text{Z} \end{array}$
6	13.0 > 15.0	$\begin{array}{c} \text{X} \quad \quad \text{Y} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array} \quad (cis)$

detail. An early use of absorption bands, which are now assigned to C—H bendings about the C=C group, was to determine whether the C=C is an internal or a terminal group; if terminal, whether it is an isopropenyl, isopropylidene, etc. The absorption bands used for these analyses and the C—H bending vibrations correlated with each of them are given in Table 63.

Jackson *et al.* (227) reported the results of infrared spectral studies on conjugated and nonconjugated isomers of methyl linoleate in the region of olefinic C—H bending. They found that a weak band with maximum at $10.95\ \mu$ is characteristic of nonconjugated *cis,cis*-linoleate and a very strong band at $10.12\ \mu$ is characteristic of conjugated *trans,trans*-linoleate, in confirmation of a similar correlation previously reported by Gamble and Barnett (184). Jackson *et al.* also reported that the spectrum of conjugated *cis,trans*-linoleate exhibited two maxima, namely, a strong band at $10.18\ \mu$ and a weaker band at $10.52\ \mu$.

Ahlers *et al.* (228) published a detailed quantitative study of 19 fatty acids including monounsaturated, and conjugated and nonconjugated polyunsaturated compounds. They confirmed the earlier work regarding the positions of band maxima for conjugated and nonconjugated polyunsaturated acids. They also reported data for the absorptivity of each acid, which agreed reasonably well with the values for the few acids for which previous data were available.

These authors accounted for the position of maxima in the spectra of conjugated acids containing *trans*-bonds by postulating a hypsochromic shift from the position of the isolated *trans*-band at $10.34\ \mu$, a shift which is small but significant and consistent with the effect of conjugation on the C—H deformation frequency of the system. O'Connor (177) postulated that a *cis*-bond produces a somewhat smaller hypsochromic effect, and thus he was able to account almost completely for the experimentally observed wavelength positions of the maxima which for the various double-bond systems are as follows: isolated *trans*, 10.34 ; *cis,trans*-conjugated, 10.17 ; *trans,trans*-conjugated, 10.12 ; *cis,cis,trans*-conjugated, 10.11 ; *cis,trans,trans*-conjugated, 10.09 ; *trans,trans,trans*-conjugated, $10.06\ \mu$.

The shift from the position of an isolated *trans*-band is least for conjugation with a single *cis*-bond, somewhat greater for conjugation with a single *trans*-bond, still greater for conjugation with both a *cis*- and a *trans*-bond, and greatest when conjugated with two *trans*-bonds. All of these *trans*-bonds give rise to absorption bands of strong or very strong intensities. This postulation did not explain the appearance of two bands in the spectra of *cis,trans*-conjugated acids which led O'Connor (177) to

postulate a similar hypsochromic effect of conjugation on the isolated *cis*-band, thereby accounting for the experimentally observed wavelength positions of the maxima of the following double-bond systems as follows: isolated *cis*, 10.95; *cis,cis*-conjugated, then unknown; *trans,cis*-conjugated, 10.53 μ . The wavelength position corresponding to *cis,cis*-conjugation was unreported at the time this postulation was made, but it was predicted (177) to be about 10.7 μ . All of the bands in the last-mentioned system have been found to be weak or very weak in intensity. The hypsochromic effect in the *cis*-system is somewhat greater than in the *trans*-system, but this is consistent with the greater variation observed in the position of isolated *cis*-bands, indicating a greater sensitivity to "molecular environment." It should be noted that in order to determine accurately the positions of these maxima an instrument of high resolving power is essential.

Crombie (229) published the spectra of several esters and alcohols including that for 2,4-decadienol, which exhibits weak bands at 10.15, 10.51, and 10.78 μ . The first two of these bands would indicate impurities of *cis,trans*-conjugation, a possibility indicated by the author. The band at 10.78 μ is that postulated for a *cis,cis*-conjugated system. Its intensity is, however, very weak. Allen (230) failed to find any bands in the spectra of *cis*-10,*cis*-12-octadecadienoic acid in the region 10.00 to 11.00 μ which might have value for diagnostic purposes. It is very probable that this may also apply to most, if not all, of the bands in the *cis*-system.

Ahlers *et al.* (228) published a detailed mathematical treatment for the quantitative estimation of isolated *trans*-unsaturated acids in the presence of *cis*-unsaturated and saturated acids, and applied it to the analysis of a mixture of elaidic and oleic acids resulting from the elaidinization of oleic acid. The method is essentially the same as that previously described by Shreve *et al.* (225). The analysis of mixtures containing conjugated *cis*- and *trans*-polyunsaturated, *cis*- and *trans*-monounsaturated, and saturated components for isolated *trans* was considered, and illustrated by application to a mixture which may be assumed to arise during the dehydration of castor oil. From the data presented by Ahlers *et al.* it would seem possible to extend the method to the quantitative determination of other components such as conjugated *cis,trans*- or conjugated *trans,trans*-dienes.

The infrared spectrophotometric method for the determination of isolated *trans*-bonds was compared with the lead salt-alcohol method of determining *trans*-octadecenoic acid. The former method was found to be more rapid, specific, and accurate (231,232) than the latter. The spec-

trophotometric method has been applied in the analysis of various natural fat products. Swern *et al.* (233) found that freshly rendered, edible beef fat, edible oleo oil, and oleostearin obtained from it, contained substantial quantities (5 to 10%) of *trans*-material which they believed to be comprised mainly, if not exclusively, of monoenes. *Trans*-9-octadecenoic (elaidic) and *trans*-11-octadecenoic (vaccenic) acids were isolated from oleo oil, the former apparently for the first time. Vaccenic acid, prepared from beef tallow was shown to be *trans*-11-octadecenoic acid by comparison of its infrared spectra with that of oleic and elaidic acids (234).

Hartman *et al.* (234a) found *trans*-acids in fats of ruminants, but, with the exception of the pig, not in the fats of nonruminants. *Trans*-acids in the fat of pigs was attributed to ingested fat present in the skim milk in their diet. These authors postulated mechanism for the formation of *trans*-acids in ruminant fats based on the observation of Reiser (234b) that ruminant bacteria hydrogenate linolenic to linoleic acid. Since hydrogenation of unsaturated acids is accompanied by partial isomerization, it could account for the presence of *trans*-isomers in the fat of ruminants. Butterfat was shown by Cornwell *et al.* (234c) to contain from 5.0 to 9.7% *trans*-acids, primarily *trans*-octadecenoic and *trans*-octadecadienoic acids with, possibly, small amounts of other *trans*-polyethenoic acids. The "oleic" acid of butterfat contains 14 to 20% of *trans*-isomers, probably a mixture of vaccenic acid and other positional *trans*-isomers.

The absence of the $10.3\ \mu$ band in the infrared spectra of C_{16} - and C_{18} -tetraene acids isolated from fresh water alga, *Chlorella pyrenoidosa*, was used by Paschke and Wheeler (235) to prove that they did not contain *trans*-double bonds. In an investigation of the unsaturated alcohol fraction of the oil from the fish, *Lacemonema Morosum*, Komori and Agawa (236) relied on the spectral band at $10.4\ \mu$ to confirm the structure of the two alcohols as *cis*-11-docosenol and *trans*-11-docosenol. Khan and Brown (237) have shown, by infrared spectral examination of coffee oil, that it contains no *trans*-acids.

Infrared spectrophotometry has also been used to affirm or disprove the presence of *trans*-acids in synthetic compounds. Ahmad *et al.* (238) synthesized *cis*-11- and *trans*-11-octadecenoic acids and showed by comparison of the infrared curves that the *trans*-acid was identical with vaccenic (*trans*-11-octadecenoic) acid isolated by Rao and Daubert (234) from beef tallow. Fusari *et al.* (239) used infrared spectra to verify the configurations of synthetic *cis*- and *trans*-6-, 7-, 8-, 9-, and 11-octadecenoic acids. They reported absorptivities of these compounds at $10.36\ \mu$ in carbon disulfide solution.

The absence of *trans*-bonds in synthetic methyl 9,10-dideuterooleate and 8,8,11,11-tetradeutero-*cis*-9-octadecene was demonstrated by Khan *et al.* (240) and Max and Deatherage (241) from infrared absorption spectra. They used the doublet at 4.64 and 4.84 μ , arising from C—D stretching vibrations, to confirm the presence of the deuterium. Abu-Nasr and Holman (242) used infrared absorption spectra to investigate the complex mixtures produced by isomerization of polyunsaturated fatty acids and their esters with sodium amide in liquid ammonia. Observations of the C—H bending vibrations in the region 10 to 11 μ showed that the reaction products of methyl linoleate were mainly *cis,trans*, with small amounts of *trans,trans*-compounds. The product from methyl linolenate was found to be more complex and contained an isolated *cis*-monoene, a *trans,trans*-conjugated diene, all *trans*-conjugated trienes, all *cis*-conjugated trienes, and possibly *cis,cis,trans*-compounds.

The method of Shreve *et al.* (225) has also been found useful in the elucidation of *cis,trans*-structure. Of the eight possible isomeric *cis,trans*-9,11,13-octadecatrienoic acids only three have been found. The stereo-isomeric configurations of all three have been established, mainly by means of infrared absorption data, and these were subsequently confirmed by synthesis.

Toyama and Tsuchiya (242a) reported the presence in pomegranate seed oil of an isomer of eleostearic acid (m.p. 43.5–44°C.) which they called puniic acid and a second stereoisomer (m.p. 35–35.5°C.) from the seed of karasu-uri (*Trichosanthes cucumeroides* Maxim), called trichosanic acid (242b). These authors later reported the isolation of trichosanic acid from balsam-pear seed oil (*Momordica charantia*) (242c). Toyama and Uozaki (242d) confirmed the presence of puniic acid in pomegranate seed oil, but failed to find trichosanic acid in the seed oil of either karasuri-uri or balsam pear. In 1949 Soni and Aggarwal (242e) reported the separation of trichosanic acid (m.p. 34–35°C.) from the seed oil of the snake gourd, *Trichosanthes anguina*.

From an examination of the infrared absorption spectra of pomegranate seed oil, Ahlers and McTaggart (243) concluded without isolating puniic acid that it was the *cis,cis,trans*-isomer of eleostearic acid. Later, Ahlers *et al.* (244) examined the absorption spectra of the purified acid from the same source and concluded that it confirmed the assigned configuration. Ahlers and Dennison (245) examined the so-called "trichosanic" acid from Japanese snake gourd oil (*Trichosanthes cucumeroides*) and showed by means of absorption spectra that it was identical to puniic acid from pomegranate seed oil and therefore has either a *cis,cis*-

trans- or a *trans,cis,cis*- configuration which probably cannot be differentiated by infrared absorption spectra.

Tolberg *et al.* (245a) pointed out that of the eight possible *cis,trans*-isomers of 9,11,13-octadecatrienoic acids only six spectroscopic species would be expected and that three of these, namely, α -eleostearic, β -eleostearic, and punicic, can be equilibrated with iodine and light. Paschke *et al.* (31) and Bickford and co-workers (32) used infrared spectra of the pure eleostearic acids, their maleic anhydride adducts, and other derivatives to establish the correct geometric structure of α -eleostearic acid as *cis,trans,trans* and the β -isomer as *trans,trans,trans*; these structures were subsequently confirmed by Crombie and Jacklin (245b) by synthesis.

Tolberg *et al.* (245a) suggested that the infrared absorption spectra of punicic acid indicated a *cis,trans,cis*-configuration rather than the *cis,cis,trans*-structure suggested by Ahlers *et al.* (243-245). This suggestion was confirmed by the total synthesis of punicic acid by Crombie and Jacklin (245b). Thus, the configurations of the three isomeric 9,11,13-octadecatrienoic acids have been definitely established.

Crombie and Jacklin also examined the so-called "trichosanic" acid reported to be present in Japanese snake-gourd oil and proved that it was impure punicic acid. The observed differences in melting point and lower absorptivities compared to punicic acid were accounted for by the presence of about 4% palmitic and 16% stearic acids. Thus, the trichosanic acids are not unique identities but impure punicic acid.

Gupta *et al.* (246) and Aggarwal (247,248) used infrared absorption spectra to prove that α -kamolenic acid from kamala oil and its β -isomer have *cis*-9,*trans*-11,*trans*-13 and *trans*-9,*trans*-11,*trans*-13-configurations, respectively. Crombie and Taylor (249) and Ahlers and Gunstone (250) have also shown by similar methods that these two isomers have the same *cis,trans*-configurations as α - and β -eleostearic acids. The former workers also showed by means of infrared absorption curves that the kamolenic acids are hydroxy and not keto compounds.

(e) Application to Hydrogenated Products

Correlations of infrared absorption data and C—H deformation vibrations about C=C bonds have been applied to study the effects produced by selective hydrogenation of unsaturated fatty acids and related materials. Lemon and Cross (251) showed, by the appearance and the intensity of the maximum at $10.3\ \mu$ in the infrared spectra of the hydro-

genated products, that hydrogenation is accompanied by a *cis-trans*-isomerization in unsaturated fatty acids. The hydrogenation of methyl α -eleostearate was followed by infrared spectra by Woltemate and Daubert (252) who observed that the principal changes consisted of the disappearance of the band at $10.0\ \mu$, which was later shown to arise from *trans,trans*-conjugation, and of the appearance of the band at $10.3\ \mu$ characteristic of isolated *trans*-bonds. According to Rebello and Daubert (253), partial hydrogenation of methyl linolenate yields a mixture of at least three isomers, namely, 8,14-, 9,15-, and 10,14-isolinoleic acids. Infrared absorption measurements indicate a *trans*-configuration for at least one of these double bonds.

Benedict and Daubert (254) used infrared spectra to show that the 8- and 9-octadecenoic acids, produced during hydrogenation of triolein, are *trans*-isomers, and Lemon (255) showed graphically the formation and disappearance of *trans*-double bonds during the hydrogenation of vegetable oils. Sims and Hilfman (256) repeated some of this work and extended it to animal fats. They found that conditions which favor selective hydrogenation of glyceride oils also favor the development of *trans*-isomers and that unusually high percentages of *trans*-linkages develop during hydrogenation of tallow.

Feuge and co-workers (257) reported a quantitative study of the hydrogenation of methyl oleate and triolein. Infrared absorption curves were obtained for samples withdrawn periodically during the hydrogenation, and measurements were made of the isolated *trans*-band appearing at $10.3\ \mu$. These studies showed that during the hydrogenation of methyl oleate: (a) *trans*-isomers are formed at very rapid rates, as much as 38% being formed during the interval in which the first 10% of methyl stearate is formed; (b) the rate of formation of *trans*-isomers is increased by increasing the temperature, increasing the concentration of catalyst, and decreasing the degree of dispersion of hydrogen during the hydrogenation; and (c) the hydrogenation of methyl oleate results in establishment of an equilibrium between *cis*- and *trans*-isomers. Irrespective of the conditions employed, the concentration of the *trans*-isomer was always 67% calculated on the basis of total unsaturated constituents. During hydrogenation of triolein, *trans*-isomers are formed at a slightly slower rate. An equilibrium is established between *cis*- and *trans*-isomers, but at values less than 67% *trans*-constituents. The equilibrium concentration was found to vary with the conditions of hydrogenation.

A similar study was made of the hydrogenation of methyl linoleate and cottonseed oil (258). Isolated *trans*-isomers were calculated on the as-

sumption that the absorptivities of the isolated *trans*-bands at $10.3\ \mu$ are additive. Analysis of the infrared curves (Fig. 24) showed: (a) a pro-

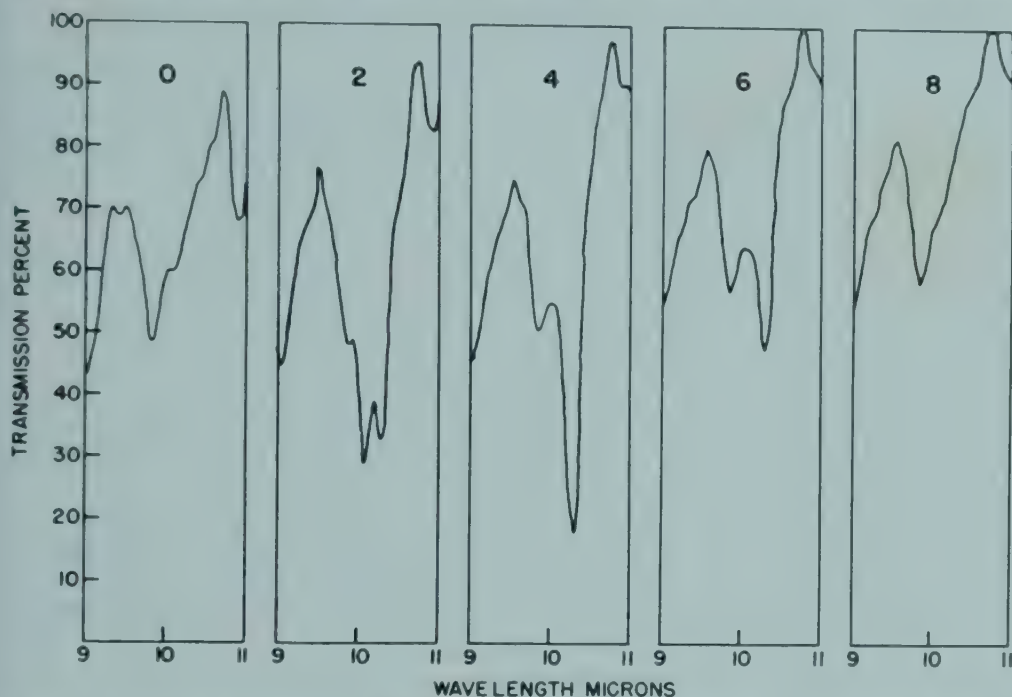


Fig. 24. Infrared absorption spectrum of methyl linoleate in the region of *trans*-absorption during hydrogenation of ester (257).

gressive decrease in the intensity of the band at $10.95\ \mu$, arising from nonconjugated *cis,cis*-bonds; (b) early appearance of bands at 10.1 and $10.3\ \mu$ attributed to *trans,trans*-conjugation, and to isolated *trans*-bonds, respectively; and (c) very rapid disappearance of conjugation and slower decrease of isolated *trans*-bonds as the hydrogenation proceeds toward formation of methyl stearate. Maximum amounts of both diene conjugation and isolated *trans*-absorption occurred during hydrogenation with increase in temperature, increase in the concentration of catalyst, and decrease in the dispersion of hydrogen. Swicklik *et al.* (259) used the method of Shreve *et al.* (225) to determine *cis-trans*-ratios during investigations of the kinetics of the hydrogenation of triglycerides. Allen (230) and Allen and Kiess (259a) used infrared spectra to characterize the products formed during the hydrogenation of pure oleic, linoleic, and *cis-10,cis-12*-octadecadienoic acids, and methyl eleostearate. During hydrogenation of oleic acid both geometric and positional isomers were formed at the same time by a half hydrogenation-dehydrogenation re-

action. With *cis*-10,*cis*-12-octadecadienoic acid, hydrogenation occurred with equal ease at the 1,2-, 1,4- and 3,4-positions of the diene system, and hydrogenation of methyl eleostearate produced equimolar amounts of 9-, 10-, 11-, 12-, and 13-octadecenoates. See Chapter XII for additional discussion of the relation between hydrogenation and isomerization. Mabrouk (259b) investigated the presence of *trans*-acids in margarines and shortenings by means of infrared absorption spectra.

(f) *Application to Autoxidized Products*

The infrared spectrophotometric methods for determining *cis*- and *trans*-configurations have found considerable use in investigations of oxidative processes, particularly autoxidation.

Knight *et al.* (260) demonstrated with the aid of infrared spectra that *trans*-double bonds are formed during the autoxidation of methyl oleate in the presence of ultraviolet light. The increase in absorption at 10.3 μ was found to parallel the increase in peroxide value, suggesting that most of the peroxides formed are *trans*-products. The autoxidation of methyl oleate between 35° and 120°C. produces a hydroperoxido-octadecenoate, most of which has the *trans*-configuration, regardless of whether the autoxidation is conducted in the dark or in the presence of ultraviolet radiation (261). Autoxidation of methyl linoleate at 0°C. leads to the formation of about 90% hydroperoxido-*cis,trans*-octadecadienoate, while at room temperature the hydroperoxido-*trans,trans*-octadecadienoate predominates (262).

Kahn and Privett (263) reported that on autoxidation of methyl linoleate at 0°C. at least 90% of the initially formed hydroperoxide has a *cis,trans*-conjugated arrangement of double bonds. At room temperature less *cis,trans*- and some *trans,trans*-conjugation was found, indicating to these investigators that the *cis,trans*-diene is labile and that at higher temperatures a further isomerization to *trans,trans*-forms occurs. *Cis-trans*-isomerization occurs during autoxidation only in the autoxidized product and not in the unoxidized fraction (264). Of the conjugated hydroperoxides formed from normal methyl linoleate at 0°C., at least 90% were *cis,trans*-conjugated, according to Privett *et al.* (265). At higher temperatures a considerable amount of the hydroperoxide goes exclusively to the *trans*-form. The major initial product of autoxidation of both methyl linoleate and methyl linolenate is a *cis,trans*-conjugated, monomeric monohydroperoxide (266).

These infrared absorption data have established that the initial product of the autoxidation of monounsaturated *cis*-compounds is the correspond-

ing isomeric *trans*-hydroperoxide, and that autoxidation of diunsaturated *cis*-compounds yields conjugated *cis,trans*-hydroperoxides at 0°C., and conjugated *trans,trans*-hydroperoxides above room temperature.

Harrison and Wheeler (267) showed that the products formed in the reaction of methyl linoleate and methyl linelaidate with di-*tert*-butyl peroxide at 125° C. consisted largely of dehydrodimers differing in the number and configuration of conjugated double bonds. Some distillate fractions of the oxidized product were rich in *cis,trans*-conjugated compounds; other fractions consisted largely of *trans,trans*-conjugated compounds; and still others had relatively large amounts of isolated *trans*-double bond compounds.

Privett and co-workers (268) found lipoxidase inactive with respect to the oxidation of *cis*-9,*trans*-12- and *trans*-9,*trans*-12-isomers of natural linoleic acid. The principal products of the lipoxidase-catalyzed oxidation of aqueous solutions of sodium linoleate are optically active, *cis,trans*-conjugated, monomeric monohydroperoxides whether the oxidation is conducted at 0° or 20° C., or in daylight or darkness. Khan (269) showed by means of infrared spectra that the enzymic oxidation of linoleic acid with lipoxidase follows the same reactions as ordinary autoxidation, yielding 9,11- and 11,13-conjugated hydroperoxides. He found *cis,trans*- and *trans,trans*-conjugated peroxides as the major oxidation products.

Dutton (270) used infrared spectra to determine the geometric configurations of the oxidation products of fatty acids after separation by countercurrent distribution. Fritsch and Deatherage (271) used infrared spectra to determine the geometric configurations of the volatile compounds produced by the autoxidation of methyl oleate, oleic acid, and *cis*-9-octadecene.

Privett and Nickell (272) have shown that concurrent oxidation of preformed hydroperoxides may be expected to take place at all stages of the autoxidation of methyl linoleate. Infrared spectral analysis of hydroperoxides oxidized to various degrees, indicated that *trans,trans*-diene conjugation and isolated *trans*-double bonds produced in the autoxidation of methyl linoleate are related to the concurrent oxidation of the accumulated hydroperoxides. The low absorptivity observed for diene conjugation compared to that which may be expected for the exclusive production of isomeric *cis,trans*-conjugated diene hydroperoxides during the autoxidation of methyl linoleate was attributed to concurrent oxidation of accumulated hydroperoxides. Studies of the autoxidation of methyl *cis*-9,*trans*-11-linoleate showed that *cis,trans*-isomerization of the conjugated diene

took place with the concurrent production of isolated *trans*-bonds and loss of diene conjugation.

(g) *Application to Other Oxidation Systems*

Infrared spectra have been applied in investigations of the rancidification of vegetable oils, polymerization, and other oxidation reactions involving the formation and fate of hydroxyl, hydroperoxido, epoxy, carboxy, carbonyl, and similar groups. The utility of infrared spectra in such investigations has not as yet been fully explored.

Rancidification. Shreve *et al.* (197) established certain correlations to show that epoxidation of long-chain, nonterminal, *cis*-monoenoic compounds results in an absorption at $12.0\ \mu$ which they attributed to formation of an oxirane ring. The ring in the corresponding *trans*-isomer gives rise to a band near $11.2\ \mu$. If the oxirane compound is derived from a compound with terminal unsaturation, bands appear near both wavelengths. These workers (197a) also showed that the infrared absorption spectra arising from hydroperoxides, which are formed during autooxidation of unsaturated fat products and other substances, exhibit the characteristic —O—H stretching vibration at $2.8\ \mu$, arising from —O—O—H groups. These hydroperoxides also give rise to a characteristic band at about $12.0\ \mu$.

Measurements in the region of C—OH stretching, about 2.7 to $3.2\ \mu$, have been particularly useful in investigations of autooxidation and their reaction products. Dugan *et al.* (273) investigated the infrared spectra of autoxidized methyl linoleate, using lithium fluoride optics to obtain higher resolution. Two bands, both of which increased with increased peroxide value were observed. One of these bands at $2.88\ \mu$ was sharp and distinct; the other was broad with maximum about $2.92\ \mu$. Reduction of the product of oxidation with potassium iodide in chloroform-acetic acid resulted in the disappearance of the band with maximum at $2.92\ \mu$ and the appearance of a new band with maximum at $2.86\ \mu$. The band with maximum at $2.92\ \mu$ was attributed to the —O—O—H group associated by hydrogen bonding. The bands at 2.86 and $2.88\ \mu$ were attributed to —O—H stretching vibrations.

The —O—H stretching band at $2.9\ \mu$ was used by Honn *et al.* (274) to study the autooxidation of linseed oil. A nonuniform increase in the intensity of this band was noted; very slowly during an initial induction period, then very rapidly as the various oxidation reactions proceeded at accelerated rates. This increase in the intensity of the $2.9\text{-}\mu$ band during

autoxidation was accounted for by the formation of hydroperoxide, $-\text{O}-\text{O}-\text{H}$; carboxyl, $-\text{COOH}$; and $\text{R}-\text{OH}$ (alcohol or water) groups. By a combination of chemical and spectrophotometric methods the increase in the concentration of each of these groups was computed. Absorptivities were reported for three hydroxy acids. The fact that the band intensities would be greatly influenced by the degree of hydrogen bonding does not seem to have been considered in the calculations involved in the measurements at various concentrations.

Lemon *et al.* (275) found that, in the early stages of autoxidation at temperatures from 22° to 100°C ., products fractionated from autoxidized methyl esters of peanut oil fatty acids developed a band in the $3\text{-}\mu$ region. This band was attributed to the $-\text{O}-\text{O}-\text{H}$ of the hydroperoxido group. At later stages of autoxidation, two bands at longer wavelengths appeared which were attributed to decomposition of the hydroperoxide to compounds containing $-\text{O}-\text{H}$ groups. Increasing the temperature increased the rate of formation and decomposition of hydroperoxides. The presence of iron stearate in the autoxidizing system catalyzed the decomposition, but not the formation of hydroperoxides.

Investigations of $\text{C}=\text{O}$ stretching between 5.7 and $6.2\text{ }\mu$ have also been found useful in following autoxidation reactions and resulting products. There is some difficulty in resolving the various $\text{C}=\text{O}$ vibrations at about $6\text{ }\mu$, and even with the use of lithium fluoride optics, Dugan *et al.* (273) found that the absorption arising from keto and aldehyde carbonyls appeared only as indefinite shoulders on the strong bands produced by the carbonyl of the ester group. In spite of the aforementioned difficulty, infrared absorption spectroscopy has made contributions to the understanding of autoxidation reactions by the interpretations of additional bands in the vicinity of the ester $\text{C}=\text{O}$ stretching band at $5.72\text{ }\mu$, which indicate the formation of aldehydes, ketones, acids, or lactones. These bands were used to investigate (275) the products fractionated from methyl esters of peanut oil fatty acids autoxidized at temperatures 22° to 100°C . In the region of $\text{C}=\text{O}$ stretching vibration, Catravas and Krafo (276) found that autoxidation of methyl oleate and methyl linoleate give unstable alcohols which are subsequently oxidized to ketones.

According to Khan (277), the reactions in the initial stages of autoxidation of methyl linolenate are of the same type as those occurring with methyl linoleate. Chang and Kummerow (278) used infrared spectra to detect the ketonic carbonyl group at $5.83\text{ }\mu$ in the presence of the ester carbonyl group at $5.75\text{ }\mu$, thereby proving that oxidation polymers of ethyl

linoleate are linked through carbon to oxygen bonds rather than through carbon to carbon bonds.

Henick (279) followed the course of autoxidation of milk fat by observing the changes in the infrared spectra of the volatile components. An off-flavor, off-odor sample of milk was steam-distilled *in vacuo* and the infrared spectra of the distilled fractions examined in carbon disulfide solution. The spectra of fresh milk exhibited only two bands in this region, at 5.80 and 5.75 μ , and after storage the band at 5.80 μ remained unchanged, but the band at 5.75 μ shifted to 5.70 μ . After longer storage, new peaks appeared at 5.86 and 5.91 μ , and after a still longer period of storage a band with maximum at 6.10 μ appeared, and it increased in intensity as the storage period was extended. Infrared spectrophotometry was found to be more sensitive to changes than a taste panel and considerably more sensitive than peroxide value determinations.

Mechanism of Drying. Gamble and Barnett (184) probably were the first to apply infrared spectra to the investigation of the drying phenomena of oils. They published several correlations of absorption bands and vibrating groups which gave rise to them. In a preliminary study of the reactions involved in resin-bodying, Kolb and Hauser (280) found that neither Raman spectra, because of strong interfering continuous fluorescence, nor ultraviolet, because of no satisfactory differentiation, offered much promise. Infrared absorption spectra, however, particularly if measured at sufficiently high resolution, appeared to be of potential value for this purpose.

In an article published in 1955, Crecelius *et al.* (281) attributed to infrared, along with ultraviolet spectroscopy, the marked advances which had been made in understanding the oxidative reactions that are involved in drying and film-formation. They discussed in detail the changes which occur in spectral bands of oils during drying, and reached conclusions regarding interpretations of bands observed in the vicinity of 3, 6, and 10 μ as follows:

(1) In 3- μ region: The appearance and rapid increase in the band at 2.93 μ indicates the formation of an —OH group which is present either as hydroperoxide or alcoholic hydroxyl. Chemical evidence has not yet demonstrated the formation of alcoholic hydroxyls. The disappearance of the band at 3.27 μ would indicate replacement of hydrogens on the double-bonded carbon with some other radical, possibly involving vinyl polymerization.

(2) In 6- μ region: The broadening of the ester carbonyl absorption at 5.72 μ indicates the formation of additional carbonyl groups, either car-

boxylic or ketonic. Changes in relative intensities of a band about 6.0 to 6.5 μ indicate alterations in the number and arrangement of C=C linkages. The appearance of a band at 6.4 μ is apparently the result of a shift toward conjugation.

(3) In 10- μ region: Increase in absorption at 10.33 μ with corresponding diminution of the bands at 10.15 and 10.98 μ is consistent with rearrangement of C=C linkages, especially when it involves *cis-trans* isomerization.

Adams and Auxier (282) reported changes in the infrared spectra of a synthetic oil as a function of its drying time. The intensities of the absorption at about 2.8 μ , attributed to formation of the hydroperoxide group, and of a band at 3.27 μ , assigned to a C—H stretching on a carbon atom adjacent to a double bond, were followed as drying proceeded. The band at 2.8 μ increased in intensity and that at 3.27 μ decreased, until finally reasonably stable values for both were reached at about the same time. This effect would be expected if one band represents an increase in the formation of hydroperoxides, and the other, a decrease in unsaturation as drying proceeded. The slope of curve of intensity vs. drying time was of the same order of magnitude as the rate of drying. Linolenates had steeper slopes than linoleates, which, in turn, were steeper than oleates, and also were in agreement with their relative drying rates. These relationships were interpreted as support for the theory that the carbon atom, α to a double bond, is particularly susceptible to oxidation and that a methylene carbon between two double bonds is more so.

Adams and Auxier were puzzled by an apparent constant shift in the wavelength position of the band at about 2.8 μ , which is now interpreted to be not a shift in wavelength position, but the appearance of new bands at longer wavelengths arising from O—H stretching vibrations of other compounds formed during the autoxidation. These bands were incompletely resolved by their instrument. Adams *et al.* (283) interpreted their infrared absorption curves of dipentaerythritol esters of oleic, linoleic, and linolenic acids in a similar manner. In this case they found that the band at about 2.8 μ increased, and that at 3.27 μ decreased as drying progressed, which they interpreted as support for the theory that during the initial stages of autoxidation of drying oils, the first step is the formation of hydroperoxides on the carbon atom α to the double bonds.

Nicholls and Hoffman (201) investigated the infrared spectra of pentaerythritol esters of linseed oil fatty acids, blown linseed oil, heat-polymerized linseed oil, etc. The O—H stretching band at about 2.9 μ progressively increased during these processes, indicating formation of O—H

or O—O—H groups. The ester carboxy band at $5.75\ \mu$ increased and widened, indicating formation of compounds containing other C=O groups which were not completely resolved in their spectra from the ester carboxy groups. Increase in the intensity of a band at about 7.9 to $8.0\ \mu$, ascribed to C—O stretching, was attributed to either an increase in ester concentration or to the formation of epoxide. Between 10 and $11\ \mu$ a band appeared which was attributed to either *trans*-double bonds or to epoxide groups. Changes occurring during drying at elevated temperatures, or in the presence of driers, were similar but more rapid.

Paschke and Wheeler (284) used infrared spectra to follow *cis-trans* changes during (a) inter- and intramolecular polymerization of heat-bodied linseed oil; (b) thermal polymerization of methyl linolenate and α - and β -eleostearates; and (c) cyclization of eleostearic acid. Kronstein (285) described the application of infrared spectroscopy to the study of drying oils and certain plastics. The spectra were limited to the region of 9 to $11\ \mu$ and no correlations of band maxima with vibrating groups were reported.

Polymerization. The thermal reaction products of methyl linoleate hydroperoxide, consisting of monomers, dimers, and trimers, were investigated with aid of infrared absorption by Williamson (286). The monomeric material consisted of methyl hydroxy- and keto-linoleate. Dimers were described which retained a large proportion of the original unsaturation of the linoleate monomer, but half of the double bonds were conjugated. Other dimers were described which were linked by carbon-carbon bonds and had a low degree of unsaturation, but contained an appreciable amount of —O—H groups. The trimeric substances appeared to consist of two monomers linked by carbon-carbon bonds and then to another monomer by carbon-oxygen bonds.

Wheeler (287) also reported on the thermal polymerization of esters of isomeric linoleic and linolenic acids. Dimerization of the nonconjugated linoleic isomers were reported to involve, first, conjugation of the double bonds, followed by reaction with a nonconjugated compound through a Diels-Alder addition in which one of the nonconjugated double bonds acts as the dienophile. Trimers were probably formed by the conjugated diene reacting with a double bond of the dimer. *Cis,trans*-conjugated isomers were reported to polymerize about six times more rapidly than nonconjugated compounds, and *trans,trans*-conjugated isomers five times more rapidly than the *cis,trans*-conjugated isomers. Linolenates were found to react in a similar manner, but the rate of polymerization was much more rapid for these compounds than for the corresponding dienes.

The infrared spectra of dimeric methyl α -eleostearate, obtained by heat-polymerization of the ester in the absence of oxygen, exhibited absorption bands at 10.15 and 10.36 μ and no band at 10.52 μ . The band at 10.15 μ and the absence of a band at 10.52 μ is indicative of a conjugated *trans-trans*-configuration, and the band at 10.36 μ of the presence of isolated *trans*-bonds. According to Clingman *et al.* (288), this latter observation indicates that the central double bond of the dienophile eleostearate moiety is not involved in reaction, and that the isolated *trans*-double bond is undoubtedly the unreacted double bond of the diene-reacting eleostearic moiety. This evidence constitutes the first structural proof for the occurrence of a Diels-Alder-type reaction in the polymerization of an unsaturated fatty ester.

Drinberg and Chervinskaya (289) investigated the effect on tung, linseed, and cottonseed oils of isomerization by contact with bentonite and the silicate waste from the production of $\text{Al}_2(\text{SO}_4)_3$ at 250° C. for about 10 hours under an atmosphere of carbon dioxide. Comparisons of infrared absorption curves of the oils before and after isomerization revealed that the isomerization was produced by migration of hydrogen so that the isolated double bonds were converted to conjugated systems.

Sims (290) used infrared absorption spectra to follow the effect of addends on the mechanisms of thermal polymerization of linseed oil. Infrared curves showed that linseed oil, polymerized in the absence of addends for five hours at 280° C. had a higher content of *trans*-bonds than when heated with addends. When linseed oil was diluted to the extent of 90% with molecularly distilled mineral oil, polymerization of acyl groups occurred without interglyceride reaction (291). Complete infrared spectra of carbon tetrachloride solutions of the heated and unheated oils were compared. In the region of 10 μ two bands were observed in the spectra of the unheated oils at 10.3 and 10.7 μ , but in the spectra of the heated oils only the band at 10.7 μ was observed. No bands were observed at 10.1 μ (*trans,trans*-conjugation) or at 10.2 and 10.5 μ (*cis,trans*-conjugation). The curves were interpreted (290) as evidence that "all samples of heated oils except the zero hour sample contain *trans*-double bonds," although the 10.3- μ band (isolated *trans*) is observed only in the spectra of the unheated samples.

In 1955 Sims (292) published a review of the status of our knowledge of polymerization of vegetable oils in which he summarized the following information obtained by infrared spectroscopy:

1. From a band at 2.9 μ some form of hydroxyl group is considered to accumulate. Whether this is due exclusively to hydroperoxides or to a combination of hydroper-

oxide and hydroxyl groups has not been resolved spectroscopically. Hydroxyl formation is the debatable point.

2. From the disappearance of a band at $3.27\ \mu$, hydrogen atoms on double bond carbons are considered to be replaced by some other radical—possibly an indication of vinyl polymerization.

3. Additional carbonyl groups are formed on the basis of a broadening of the band at $5.72\ \mu$.

4. From spectral changes in the 6.0 to $6.5\ \mu$ and the 10.15 to $10.95\ \mu$ regions, changes in the number, arrangement, and geometric configuration have been deduced; conjugation and *trans*-isomerization are indicated.

5. Ultraviolet irradiation caused loss in weight and decrease in infrared absorption in the regions characteristic of hydroxyl, carbonyl, and CH_2 groups.

These conclusions probably constituted as accurate a summary of the status of the applications of infrared absorption to polymerization as could be given at that time.

Other Oxidations. Smith *et al.* (293) obtained infrared absorption curves of fractionated methyl esters of monoenoic acids from C_{10} to C_{20} of milk fat, and compared them with available spectra for pure saturated and unsaturated esters of long-chain fatty acids. Absence of a band at 2.8 to $2.9\ \mu$ indicated that no oxidation had occurred to give hydroperoxidic hydroxyls. A band at $10.35\ \mu$ indicated the formation of *trans*-bonds ranging from 14 to 27% in the monoethenoid methyl esters. Spectra of the C_{18} - to C_{20} -fractions indicated the presence of conjugation entirely of the *cis,trans*-type. The infrared spectrum of the C_{10} -fraction indicated the presence of terminal bonds between the 9 and 10 carbon atoms.

Peracetic and performic acid oxidation of linoleic acid was studied by McKay *et al.* (294). Besides isomeric sativic acids, two new oxidation products were isolated but only partially characterized. Infrared spectra established that the compound formed by oxidation with performic acid contained hydroxy groups in the chain. A weak band at about $3.27\ \mu$ indicated the presence of an unsaturated linkage or possibly a cyclopropyl group. The latter appears more probable as the spectra failed to show any evidence of unsaturation in the region of $\text{C}=\text{C}$ stretching, about 6.0 to $6.2\ \mu$, or in the region of $\text{C}-\text{H}$ bending about the $\text{C}=\text{C}$ group, between 10 and $11\ \mu$. Chang and Kummerow (295) showed, by means of infrared absorption, that the volatile odoriferous components of fresh undeodorized edible tallow were quite complex. The infrared absorption spectra revealed evidence of the possible presence of hydroxyl, carbonyl, aliphatic ether, and ester groups, conjugation, carbon-nitrogen bonding, and six-member lactone rings.

O'Connor and co-workers (198) described the infrared spectra of 10 -

and 12-hydroxystearic acids, their methyl esters, and 9,10-epoxystearic acids derived from oleic and elaidic acids. They reported absorptivities and correlations of the most prominent bands in these spectra with molecular groups most likely responsible for them. Infrared spectra were used to support a hypothesis explaining the formation of 10-hydroxystearic acid rather than a mixture of the 9- and 10-isomers upon hydrogenation of 9,10-epoxystearic acid, and to support an explanation for the gelling tendencies of 12-hydroxystearic acid as compared to the nongelling tendencies of 10-hydroxystearic acid.

Khan *et al.* (264,296) reported the results of an investigation of the photochemical oxidation of fatty acids in the presence and absence of chlorophyll. Under all of the conditions employed, the oxidation of methyl oleate and linoleate led primarily to the formation of monomeric peroxides which retained most of the unsaturation of the parent compounds. Formation of *trans*-hydroperoxides, upon autoxidation of methyl oleate, and of *cis,trans*-conjugated hydroperoxides at low temperatures; and of *trans,trans*-conjugated compounds at or above room temperature, were confirmed. In the case of methyl oleate no *cis-trans*-isomerism occurred in the unoxidized oleate, i.e., conversion of *cis* to *trans*, and formation of peroxides occurred together in the same molecule. The change from *cis,trans* to *trans,trans*, however, seems to be independent of the autoxidation of the methyl linoleate. The photochlorophyllic oxidation of methyl linoleate results in the formation of unconjugated hydroperoxides, some with *trans*-configuration.

Khan *et al.* (297) used displacement chromatography and infrared absorption spectra to identify hydroxy-reduction products of peroxides formed by six different methods of oxidation of methyl linoleate. Autoxidation at -10°C . in the dark; with a copper catalyst; with visible irradiation; and with ultraviolet irradiation—all yielded qualitatively similar products. All of the major reduction compounds exhibited *cis,trans*- or *trans,trans*-conjugation. Photochemical oxidation in the presence of chlorophyll resulted in four major products, one of which exhibited no conjugation, and contained two double bonds and one OH group per mole. The latter compound was tentatively identified as 11-hydroxylinoleate. Oxidation with lipoxidase resulted in the formation of six substances.

(h) *Elucidation of Structure*

The uses of infrared absorption spectra to establish structures of the *cis,trans*-type in fatty acids and various derivatives were discussed in

earlier sections of this chapter. Here follows a discussion of other similar applications, and also others involving the establishment or confirmation of several unusual structures which have been encountered in natural fatty acids.

Celmer and Solomons (298) adduced the structure of mycomycin and isomycomycin, using infrared spectra at several critical steps. A summary of the procedure followed by Celmer and Solomon has been given by Wheeler (204). In their search for the hypotensive principle of tung oil, Davis *et al.* (299) obtained a crystalline fraction which, with the aid of infrared absorption curves, was shown to be 9,14-dihydroxy-10,12-octadecadienoic acid.

Performic acid oxidation of sphingomyelin and related lipides was shown by Marinetti and Stotz (300) to result, first in formation of an epoxide ring at the double bond, then a hydroxyl and aldehyde group, and finally conversion, by the action of a base, to a dihydroxy compound. Absorption curves of the oxidation products revealed that (1) no C=O stretching at $5.81\ \mu$ was evident at the first stage of oxidation, and that it appeared at the second stage and disappeared in the last stage; (2) no bands appeared in the region of O—H stretching, $3.0\ \mu$, in the first stage, but a band at $3.00\text{--}3.10\ \mu$ appeared in the second stage, and increased in intensity in the third stage. The original compound exhibited a band at $10.3\ \mu$ indicating that it contained a *trans*-double bond. However, this band did not disappear on hydrogenation, but only became less intense, indicating that a portion of the absorption was due to the P—O—C group of the molecule, which also gave rise to a band at $10.3\ \mu$. Marinetti and Stotz (300) studied the spectra of lipides which contain no interfering P—O—C linkage and found that the $10.3\ \mu$ band completely disappears on hydrogenation.

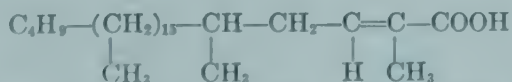
On the basis of ultraviolet spectra and hydrogenation data Ligthelm and Schwartz (300a) showed that ximenynic acid, isolated from the kernel oil from *Ximenia caffra* Send., *X. caffra* var. *natalensis* Sond., and *X. americana* var. *microphylla* Welw., contained a double bond and a triple bond. Ozonolysis indicated that the acid had the structure heptadec-10-en-8-yne-1-carboxylic acid (300b). Ahlers and Ligthelm (300c) used infrared absorption spectra to confirm this structure. The spectra of methyl ximenynate exhibited the absorption bands attributable to long-chain methyl esters as well as a band at $4.50\ \mu$ associated with acetylenic triple bond stretching, and one at $10.47\ \mu$ characteristic of C—H bending about an internal *trans*-C=C bond. Shift in position of this latter band from its usual wavelength position at $10.33\ \mu$ was attributed to conjuga-

tion with the triple bond. This configuration was later confirmed by Griger *et al.* (300d) who reported a synthesis for the acid.

Gunstone and McGee (300e) used infrared spectra to show that santalbic acid, which occurs in santalum seed oil is *trans*-octadec-11-en-9-ynoic acid. Infrared spectra of the acid they isolated from santalum seed oil was identical with the ximenynic acid synthesized by Griger *et al.*

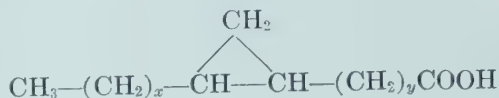
Crombie and Jacklin (300f) showed that the infrared spectra of their synthetic ($\pm$)-ricinoleic acid was identical with the natural (+)-ricinoleic acid. Kendall (300g) used infrared absorption in each step of the synthesis of DL-ricinoleic acid, and showed that the final product gave a spectra almost identical with that of methyl D-ricinoleate.

Freeman (301) and Cason *et al.* (302) resorted to infrared spectra to prove the structure of the C₂₇-phthenoic acid isolated from crude methyl phthioate. Chemical and ultraviolet absorption data indicated that the acid was a 2-alkyl-2-alkenoic acid with a second substituent in the 4 or 5 position, and a third substituent on a carbon more remote from the carboxyl. The infrared spectra exhibited a band at 6.08 μ , indicating a C=C group. The C=O band appeared at 5.91 μ , a position somewhat longer than the usual C=O stretching of saturated esters, indicating that the C=O was conjugated with the C=C group. Bands at 10.06, 12.50, 13.20, and 14.12 μ were attributed to C—H deformations about C=C groups, indicating that the C=C had at least one hydrogen atom attached to it. Comparisons with data reported earlier by Freeman (190) and the work of Sobotka and Stynler (189) on the spectra of isopalmitic and isostearic acids showed that no iso- or neo-configuration was present. The possibility of a quaternary carbon atom more remote from the carboxyl than the α -position was eliminated by absence of a band at 8.8 μ , and absence of bands at about 12.95 and 13.5 μ eliminated both ethyl and propyl groups. Consideration of bands at 7.8 and 8.1 μ and the study by Freeman (190) of the spectra of branched-chain fatty acids indicated a methyl group α to the carboxyl and a second methyl group not farther removed than the δ -position. Intensities of the methyl band at 7.3 μ indicated the presence of four methyl groups. From these considerations, coupled with chemical evidence, the structure of phthenoic acid was considered to be:



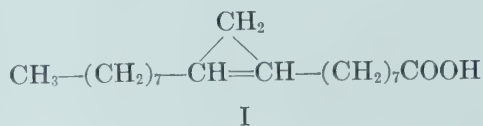
Lactobacillic acid, C₁₉H₃₆O₂, isolated by Hofmann *et al.* (303) is a saturated acid containing two less hydrogens than a normal C₁₉-saturated

acid, suggesting a cyclic structure. Infrared absorption spectra revealed a band with maximum at $9.8\ \mu$, characteristic of alkyl-substituted cyclopropanes. Hence, lactobacillic acid was considered to have a formula corresponding to:

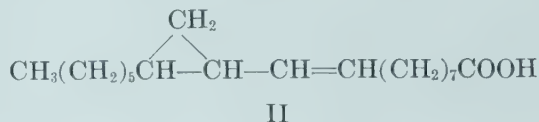


where $x + y = 14$.

Sterculic acid, $\text{C}_{19}\text{H}_{34}\text{O}_2$, isolated by Nunn (304), was shown, by appearance in the infrared absorption spectra of the band with maximum at $9.85\ \mu$, to have the structure



Verma *et al.* (304a) reported a detailed study of the infrared spectra of sterculic acid and of some of its related compounds. They concluded that the formula proposed by Nunn was not entirely compatible with observed data and proposed the formula



The compound proposed by Nunn was synthesized and its infrared absorption spectra was found to be quite different from that of sterculic acid.

Varma *et al.* (304b) supported the assignment of formula (II) to sterculic acid on the basis of the production of hexyl *n*-methyl ketone, heptanoic acid, and azelaic acid, which they obtained on oxidation of the acid with potassium permanganate. They claimed that these products of oxidation could be explained on the basis of their proposed structure, but not on one containing a cyclopropene ring [formula (I)].

Other workers who have examined the infrared spectra of sterculic acid have questioned the conclusions of Verma and co-workers. Dijkstra and Duin (304c) gave three reasons for supporting formula (I) proposed by Nunn. These reasons are as follows:

(1) The infrared absorption spectra of 2-cyclopropylpropene exhibit a band with maximum at $9.77\ \mu$. In the spectrum of 2-cyclopropylpropane this band is shifted to $9.82\ \mu$. The hydrogenation of the cyclopropene ring of sterculic acid results in a shift in a band at $9.91\ \mu$ to a band at $9.79\ \mu$

in the spectra of dihydrosterculic acid, a shift which is in the opposite direction to that encountered with 2-cyclopropylpropene. This greater displacement in the opposite direction, occurring on the conversion of sterculic to dihydrosterculic acid, is attributed to increased ring strain which has been verified in the case of the cyclopropene ring by electron diffraction measurements. As this is the shift in band position which would be expected for the cyclopropene ring, it indicates the presence of this group in sterculic acid.

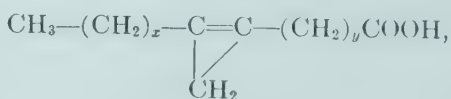
(2) The Halphen reaction, a red color developed in a solution of sulfur in carbon disulfide, is given with the seed oil of *Sterculia foetida* and with kapok seed oil, and the reaction is attended by the appearance of a band in the infrared spectra of the oils at $9.91\ \mu$. This band is not observed in the spectrum of cottonseed oil, which also gives a positive Halphen reaction, probably because the concentration of the sterculic-like acid (see Halphen acid) is below the sensitivity with which this band can be detected. When the oils are treated to cause the disappearance of the band at $9.91\ \mu$, no Halphen reaction is obtained. Neither cyclopropane derivatives nor conjugated systems give the Halphen reaction. This constitutes further evidence for the presence of the cyclopropene structure of sterculic acid.

(3) Sterculic acid polymerizes very readily, whereas the cyclopropane ring and 9,11-octadecadienoic acid are fairly stable at room temperatures. Furthermore, conjugation of two such groups would be expected to increase this stability. The extreme reactivity of sterculic acid likewise is evidence of the presence of a cyclopropene ring.

Faure and Smith (304d) could find no evidence of a band with maximum at $6.09\ \mu$, reported by Verma *et al.* in the infrared spectra of freshly prepared sterculic acid. Bands with maxima at $9.92\ \mu$ (strong) and at $5.35\ \mu$ (weak) were assigned to the cyclopropene ring, confirming the structure proposed by Nunn. As sterculic acid aged, the weak band at $5.35\ \mu$ disappeared, the band at $9.92\ \mu$ became weak, and a new band appeared at $6.07\ \mu$. The spectra now resembled that reported by Verma *et al.* Faure and Smith suggested that Verma *et al.* measured the spectra and based their postulated structure on a sample of spontaneously polymerized sterculic acid. The infrared absorption spectra was interpreted by Faure and Smith as indicating that this polymerization does not involve reaction of the C—C with the C=O of the carboxyl, but rather a splitting of the C—C linkage, opening of the ring, and reaction of the carboxyl group, as evidenced by the shift of the C—O stretching from $5.86\ \mu$ (acid) to $5.76\ \mu$ (ester.)

Faure and Smith (304d) contended that the key compound in Nunn's chemical evidence for the cyclopropene structure was the dioxo acid obtained by hydrogenation of the ozonide formed from sterculic acid and deduced to be 9,11-dioxononadecanoic acid, $\text{CH}_3(\text{CH}_2)_7\text{COCH}_2\text{CO}-(\text{CH}_2)_7\text{COOH}$. Faure and Smith prepared this compound from sterculic acid by ozonolysis in cold ethyl acetate and hydrogenation of the ozonide with 30% palladium-charcoal. They supported evidence given by Nunn for the structure of 9,11-dioxononadecanoic acid, based on chemical tests and ultraviolet absorption spectra, by showing that this structure was compatible with (a) infrared absorption spectra, (b) color tests with alcoholic ferric chloride, and (c) the fact that they were able to isolate and identify three of the four products which would be expected upon alkaline hydrolysis of a dioxo acid of this structure. A compound corresponding to this structure would not result from ozonolysis and subsequent hydrogenation of a compound containing a cyclopropane ring, conjugated to a $\text{C}=\text{C}$ group, as, for example, in the structure [Formula (II)] proposed by Varma *et al.* (304b); therefore, Faure and Smith (304d) concluded: "All the spectral and chemical evidence which exists with regard to sterculic acid supports the originally proposed structure of Nunn."

Macfarlane *et al.* (304e) isolated a biologically active C_{18} -fatty acid from *Malva verticillata* and *M. parviflora* which had previously been referred to as Halphen acid because it gives a positive Halphen color reaction. They proposed the name malvalic as more appropriate for this acid. These workers believed that the structure proposed by Nunn was preferable to that proposed by Varma *et al.* for sterculic acid; hence, in agreement with Faure and Smith, they assigned to malvalic acid the structure,



similar to Nunn's structure for sterculic acid.

Faure (304f) showed that the reaction of sterculic acid with carbon disulfide gives rise to bands in the infrared spectra with maximum at 4.88μ and at 12.95μ . The intensities of these bands increase as the red Halphen color increases. Faure did not find either sulfur or amyl alcohol essential for the Halphen test. The two infrared bands were attributed to $\text{C}=\text{S}$ stretching of the $\text{S}-\text{C}=\text{S}$ group and to a $\text{C}-\text{S}$ antisymmetrical stretching of the $\text{C}-\text{S}$ group, respectively. They could, presumably, be used as the basis of an infrared method for the determination of sterculic acid or sterculic-like acids which give the Halphen color reaction.

Balakrishnan *et al.* (304g) examined the infrared spectra of twenty sandalwood oils all of which exhibited bands at $3.2\text{--}3.3\ \mu$ and at $9.8\text{--}10\ \mu$, characteristic of the cyclopropane ring. Acetylation, to remove any interference from the O—H vibrations, provided a method for the quantitative estimation of the content of cyclopropane ring and a criterion of the oil quality.

Additional weight in favor of the formula (I) proposed by Nunn for sterculic acid was published almost simultaneously by Brooke and Smith (304h) and by Lewis and Raphael (304i), and shortly thereafter by Narayanan and Weedon (304j). These groups of workers achieved the total synthesis of 9,11-dioxononadecanoic acid and showed that the synthetic material was identical with the dioxononadecanoic acid obtained by Faure and Smith (304d) on degradation of sterculic acid.

Although the preponderance of evidence appears to favor the cyclopropene structure for sterculic acid [formula (I)] as originally proposed by Nunn (304), Varma and colleagues continue to support a cyclopropane ring structure [formula (II)]. In 1957, they (304k) proposed to estimate the content of sterculic acid in the seed of *Sterculia foetida* Linn. by means of the band at $9.92\ \mu$ in the infrared absorption spectra of this acid, which they (304l) maintained is characteristic of a cyclopropane ring. These workers pointed out that, with their proposed structure, the cyclopropane ring behaves toward heat and certain reagents more or less like an olefinic double bond. The cyclopropane conjugated with the $\text{C}=\text{C}$ results in a compound which they believe behaves like a typical diene-conjugated system, and that it accounts for the striking gelation properties of the seed oil of *Sterculia foetida*.

Several workers have been interested in the structure of sterculic acid mainly because the acid gives the Halphen color reaction for cottonseed oil. Gunstone (304m), for example, has attributed the Halphen reaction to the presence of an acid in cottonseed oil in minute proportion, which contains a cyclopropene ring.

An infrared absorption curve was used by Khan (305) to show that stearolic acid contains a triple bond. A weak absorption only, with a maximum at $4.42\ \mu$ was interpreted as indicating that the triple bond was flanked on either side by balanced groups, $\text{CH}_3\text{—}(\text{CH}_2)_7\text{—C}\equiv\text{C—}(\text{CH}_2)_7\text{COOH}$.

Walborsky *et al.* (306) used infrared spectra to confirm the absence of an allene structure conjugated with an acetylenic group ($5.13\ \mu$) and the absence of *trans*-isomers ($10.3\ \mu$) in their total synthesis of linoleic acid. Friedberg *et al.* (307) used infrared absorption spectra in an attempt to

characterize an unknown acid separated from brain extract by chromatography. Infrared spectra at the regions of C=O stretching ($6.0\ \mu$) and of C—H deformation about a *trans* C=C ($10.0\ \mu$) were studied in particular by Crombie (308) to verify the structure of *cis*- and *trans*-isomers of *N*-isobutylundeca-8,7-diene-1 carboxyamides.

By analysis of the infrared absorption curve, Festenstein *et al.* (309) were able to show that a constituent from the unsaponified portion of animal tissue lipids is a steroid with a chromophoric group 8(9)-ene-7,11-dione. Fairbairn (310) showed that ascaryl alcohol is the major constituent from the lipids of female reproductive organs in *Ascaris lumbricoides* and presented a hypothetical structure for the compound based largely on infrared absorption spectra. Goldblatt *et al.* (311) used infrared absorption to confirm the structure of β -lactyl- α,γ -dipalmitin (2-lactyl-1,3-dipalmitin).

Ultraviolet absorption indicated that the acid isolated by Silk and Hahn (312) from South African pilchard oil was a nonconjugated tetraene; alkali-isomerization indicated that all double bonds were methylene interrupted. Infrared absorption spectra, which showed no evidence for C—CH₃ groups and exhibited the presence of the vinyl, CH=CH₂—, group, were used in conjunction with elementary analysis and permanganate oxidation to prove that the structure of the acid is, HOOCCH₂—CH=CH—CH₂—CH=CH—CH₂CH=CH—(CH₂)₄CH=CH₂.

In summary it may be said that infrared absorption has become an established tool for obtaining preliminary information or final conformation of molecular structure. An infrared absorption curve should properly be considered necessary confirming evidence for the support of any proposed structure. A proposed molecular formula cannot be considered as acceptable so long as any unexplained anomalies exist between the infrared absorption curve and the proposed structure.

(i) Miscellaneous Qualitative Applications

Kuhrt *et al.* (196) used infrared absorption spectra to identify the monoglycerides isolated from lard and bread and from the triglycerides in the intestinal tract of humans, essentially by direct fingerprint comparisons of the spectra. Brokaw *et al.* (313) used infrared spectra to characterize 2-monoglycerides isolated from commercial monoglycerides and from other sources. Baer (199) discussed the spectra of three synthetic L- α -lecithins (dimyristoyl, dipalmitoyl, and distearoyl) which constitute a homologous series of pure phospholipides, and Baer *et al.* (199a)

did likewise for the spectra of distearoyl-, dipalmitoyl-, and dimyristoyl-cephalin.

"Breathing" vibrations of the aromatic ring were used by Brunner and Tucker (314) to show that interpolymerization of styrene occurred in the presence of tung oil, but not in the presence of dehydrated castor oil. Harrison and Daubert (315), by means of infrared absorption spectra, showed that pure methyl isolinoleate has one or probably two isolated *trans*-double bonds. Autoxidation of this compound gave derivatives of saturated and unsaturated carbonyls similar to those obtained from soybean oil, indicating that isolinoleic acid may be one of the precursors of reversion compounds. Two of the autoxidation products, 2-hexanol and 2,6-decadienol, were identified by direct fingerprint comparison of the spectra of their dinitrophenylhydrazones with the dinitrophenylhydrazones of authentic samples.

Infrared absorption spectra have been used to confirm the structure of alkane-1,2-diols isolated from the unsaponifiable fraction of wool wax (316); to identify the component alcohols in polymeric esters by direct fingerprint comparison of their spectra with those of commercial alcohols as standards (317); and to identify dicarboxylic acids in polymeric esters by refluxing the esters with benzylamine and identifying the resulting dibenzyl amides by direct fingerprint comparison with a standard set of dibenzyl amides prepared from monomeric esters (318). Hoffman *et al.* used infrared absorption spectra to follow the reaction and help identify the products formed in preparing the adducts of α - and β -eleostearic acids and β -propiolactone (319), and of acrylonitrile and fumaronitrile (320).

The infrared spectra of dipalmitoleyl-L- α -glyceryl-phosphorylcholine from yeast was compared with that of its hydrogenation product, dipalmitoyl-L- α -lecithin, and with the spectra of palmitoleic acid by Hanahan and Jayko (321). The spectra of the two lecithins were similar, the unsaturated compound exhibiting a band at 14.7μ , which was not observed in the spectra of the saturated compound, and hence attributed to a *cis*-double bond. The infrared spectra of palmitoleic acid is very similar to that of oleic acid and has a *cis*-band at 13.17μ , and no evidence of a *trans*-band at 10.36μ . Renkonen and Koulumies (322) compared the spectra of serum lipides from normal individuals and from young and old diabetics with the spectra of pure lipides.

Gold (323), by means of infrared spectra, followed the oxidation of methyl elaidate and methyl oleate with gaseous oxygen at 120°C . in the presence of a uranium catalyst. The initial step of the oxidation was the

formation of an unsaturated hydroperoxide, the concentration of which first increased and then decreased. This was followed by an intermediate stage during which unsaturated ketones, epoxides, and acids were produced, the concentration of which increased to a maximum and then decreased. The final stage was the appearance of hydroxyl groups, the concentration of which increased steadily to a limiting value.

Miller and Shreve (324) could find no satisfactory chemical method for the estimation of the ratio of urea formaldehyde to melamine resin in a paint vehicle comprising both of these resins admixed with an alkyd resin. They developed a method based on infrared absorption employing bands at 5.8μ (ester carbonyl), at 6.1μ (amine carbonyl), and at 12.25μ (triazine ring). Absorptivities at these three wavelengths were used to develop multicomponent equations for the simultaneous determination of the three components.

Gore and Waight (325) described a method for identifying a fatty acid by means of the ratio of the methylene group near 3.41μ to that of the methyl group about 3.38μ . The method requires an instrument capable of resolving bands which are separated by only a few hundredths of a micron. Jones and Sandorfy (325a) cited several examples of the application of infrared to the elucidation of the molecular structure of fatty acids and their derivatives.

(j) Miscellaneous Quantitative Applications

The method of Shreve *et al.* (225) for the determination of isolated *trans*-acids and extensions by Ahlers *et al.* (228) are the only completely described quantitative methods of infrared spectroscopy which have been applied to fatty acid chemistry. However, studies of the infrared absorption of several compounds have suggested many potential quantitative methods. For example, Ahlers and McTaggart (326) recommended the use of infrared spectroscopy for the quantitative determination of hydroxyl, ketone, and ester groups and described its application to the analysis of autoxidized materials. They avoid hydrogen-bonding effects by use of very dilute solutions. Hydroxyl values determined by the infrared method agreed very well with those obtained with the acetic anhydride method; ketone content agreed very well with the results of a hydroxylamine method; and the concentration of ester carbonyl was very close to values obtained by a chemical saponification procedure.

Thomas (327) showed that it was possible to determine quantitatively the concentration of two groups, e.g., alcoholic hydroxyl and carboxyl,

even when they are present in the same molecule, as in ω -hydroxypalmitic acid. In very dilute solution, the —OH stretching vibration occurs at $2.74\ \mu$, the position of free —OH . The —OH stretching of the COOH group, however, even in very dilute solution, is bonded, probably as a single-bridged dimer and the band appears at $2.84\ \mu$.

A method, based on infrared spectra, for the determination of the position of double bonds was suggested to van Tamelen and Shamma (328) from an investigation of the spectra of iodolactonized acids. A band at $5.6\ \mu$ in the spectra of iodolactone indicated that the starting acid was probably β,γ - or γ,δ -unsaturated, while absorption at $5.75\ \mu$ demonstrates the probable presence of a δ,ϵ -double bond.

O'Connor *et al.* (329) compared the infrared spectra of mono-, di-, and triglycerides and found three regions of the spectra in particular which might be useful for purposes of analysis. The O—H stretching region at about $3.0\ \mu$ could, by the complete absence of the characteristic C—H stretching vibration band, be used to confirm the absence of mono- or diglycerides in a preparation of triglycerides. In the region of C—O stretching, about $9\ \mu$, monoglycerides exhibit a characteristic band at $9.5\ \mu$ and diglycerides a band with maximum at $9.6\ \mu$. Triglycerides exhibit no bands at these wavelengths. Both of these bands were assigned to C—O stretching of α -substituted secondary alcoholic groups, the difference in wavelength position of the maxima being accounted for by the difference in the α -substituent groups.

O'Connor *et al.* (329) showed that qualitative detection and, probably, quantitative determination of mono-, di-, and triglycerides in admixtures could be made by use of these bands. In the region of C—H bending about *trans*- C=C groups, above $10\ \mu$, triglycerides of mixed long- and short-chain fatty acids, e.g., acetoolein, dibutyroolein, etc., exhibit a band with maximum at $10.4\ \mu$. The intensity of this band must be considered in applying the method of Shreve *et al.* (225) to determine the concentration of *trans*-isomers in such triglycerides by including in the "background" corrections values obtained from the spectra of the appropriate pure triglycerides.

Freeman *et al.* (330) compared the spectra of lipoproteins isolated from human blood serum with the spectra of such reference compounds as vegetable oil, ovalbumin, cholesteryl, egg lecithin, etc. They reported correlations of the observed bands with the lipoprotein components and suggested methods for quantitative analyses. The C—O ester carbonyl band could be used to determine lipide content; the band at $9.5\ \mu$ to

determine unesterified cholesterol; and the protein content by the ratio of the intensities of the absorption bands at 5.8 and 6.1 μ .

Considerable use of infrared spectra was made by Marinetti and Stotz (300) in their investigation of the structures of phospholipides. They reported bands at 10.3 μ arising from the covalent phosphate, P—O—C group, in saturated lecithin and for the *trans*-double bond, and for the P—O—C group in unsaturated phospholipides. A band at 9.2 μ was also believed to arise from P—O—C vibration, and one at 8.2 μ from a C—O—C linkage. All the phospholipides exhibited a band near 13.80 μ , attributed to long carbon-carbon chains, and an unassigned band at 14.4 μ . Glycerophospholipides exhibit a very strong ester C=O stretching band at 5.70 to 5.78 μ and sphingolipides are characterized by a strong C=O stretching band at 6.1 μ . In addition, the latter compounds exhibit the N—H and O—H stretching bands in the region 3.0–3.4 μ . The glycerophospholipides and the sphingolipides can be determined quantitatively in admixture by measurements of the bands at 5.76–5.78 and at 6.1 μ .

Bezman and Browning (331) used the band at 5.8 μ to measure quantitatively the oil content of copolymers made in aqueous emulsions of styrene with linseed or soybean oils. They showed that untreated, non-conjugated oil does not form polymers, but that copolymerization does occur in treated, i.e. blown, thermally polymerized, or oxidized oils containing conjugated linkages. They concluded that "in systems as complex as natural drying oils this (*infrared spectra*) may indeed be the only reliable method for determining reaction of oil and the changes in chemical groups."

The effect of different fatty acids on the polymerization of styrene was investigated by Harrison and Tolberg (332). They established a multi-component system for analysis of the benzoate, fatty ester, and polystyrene. Methyl and ethyl benzoate, measured by the band at 5.70 μ , were used as the reference standard for the benzoate, and methyl stearate, measured at 5.75 μ , was used as the reference standard for the fatty acid esters. Heat-polymerized, carboxyl-free polystyrene was used as the reference standard for polystyrene. Measurements were made at only the two carboxy frequencies because the contribution of polystyrene was small and constant. Methyl stearate and methyl oleate acted largely as diluents, slowing the polymerization rate slightly, but not reducing the molecular weight of the polymer and not reacting with the polymer to any appreciable extent. Methyl linoleate and linolenate acted as chain terminators, reducing the molecular weight and the rate of polymerization, but entering into the polymer only to the extent of 2 to 3 moles per mole of polymer. The conjugated linoleates copolymerized with the styrene

without affecting the molecular weight or rate of polymerization and combined to the extent of 12 to 15 moles per mole of polymer.

Jaffe and Pinchas (333) described a method for determining dipentaerythritol in the presence of pentaerythritol by use of a band at $8.93\ \mu$, due to $-\text{CH}_2-\text{O}-\text{CH}_2-$. This absorption band occurs only in the spectrum of dipentaerythritol.

The development of quantitative methods involving infrared absorption spectroscopy have lagged behind applications in qualitative detection and elucidations of molecular structure mainly because of the lack of reliable quantitative data upon which such methods must be based. This lack arises from the unavailability of highly pure reference compounds. The need for such compounds derives from the fact that quantitative infrared absorption data cannot be interchanged between laboratories with any degree of precision. Values of specific absorptivities obtained from measurements on pure compounds in the infrared region are critically dependent upon the entrance slit-width and the physical characteristics of the particular instrument with which they were determined. Hence, even when obtained from a single preparation of adequate purity, quantitative infrared absorption data are not available for general application to a proposed quantitative procedure.

Williams (334) discussed in considerable detail the problem of interchanging infrared absorption data, and Shreve *et al.* (185) suggested that it may not be necessary for every laboratory to redetermine every absorptivity required for a specific quantitative determination. They suggested redetermination of a critical coefficient from a primary standard and recalculation of others by calibration.

(k) Infrared Absorption in the Solid State

Sinclair *et al.* (187,188) emphasized the fact that the most remarkable feature in the spectra of crystalline acids and esters is a progression of bands between about 7.4 and $8.5\ \mu$, spaced at approximately equal intervals. These bands are not observed in the spectra of solutions, but only in those of crystalline films, Nujol mulls, potassium bromide disks, etc. They are undoubtedly associated with methylene wagging and/or twisting vibrations. Jones *et al.* (335) studied these band progressions and found that the number of bands in the progression is proportional to the chain length of the fatty acid or ester. This is illustrated in Figure 25 for the spectra of potassium bromide disks of crystalline acids with even numbers of carbon atoms from caproic to stearic (C_{12} to C_{18}). It may

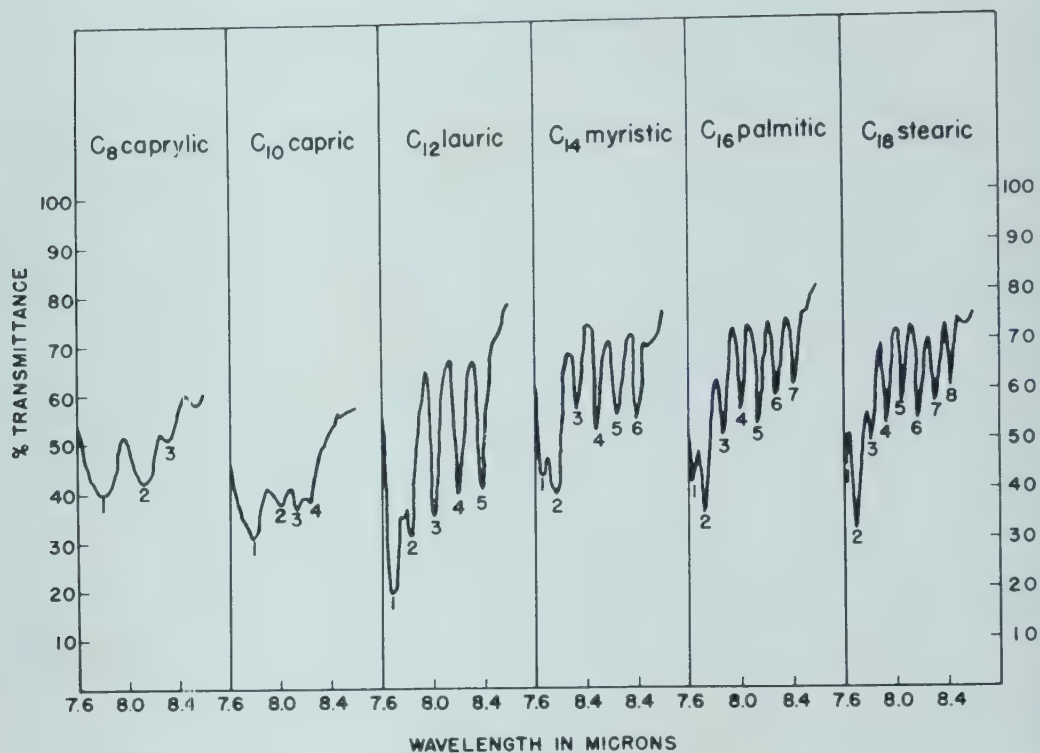


Fig. 25. Infrared absorption spectra of potassium bromide disks of saturated acids. Note increase in number of progression bands with increase of number of carbon atoms in the chain.

be seen from this figure that the chain length of these compounds can be calculated from the formula: No. carbon atoms = $2 \times$ No. observed absorption bands $+ 2$.

Meyer and Schuette (336,337) measured the infrared absorption spectra of the crystalline phase of over three hundred long-chain aliphatic compounds including hydrocarbons, acids, alcohols, dicarboxylic acids, halides, amines, amides, nitriles, etc., and concluded that the individual bands in the progression arise from inductive effects of the terminal polar group. The number of bands depends upon the number of methylene groups in the chain. For every two methylene groups, one progression band results. Progression bands are not found in hydrocarbons. In the spectra of aliphatic monocarboxylic acids, the number of bands increases with the number of carbons in the chain, but the intensities of the bands decrease. In dicarboxylic acids the number of progression bands is the same as in the monobasic compounds with the same number of carbon atoms, but the intensities are considerably greater.

Erik von Sydow (338) reported the infrared spectra of Nujol mulls of different crystal forms (polymorphs) of a number of normal fatty acids. He found that there are easily recognizable differences in the spectra of the different crystalline modification of the same acid at $5.9\ \mu$, the $\text{C}=\text{O}$ stretching vibrations, and near $7.0\ \mu$, CH_2 deformation. At 7.7 to $8.5\ \mu$, i.e., in the region of the progression bands, it was found that the exact positions of the absorption peaks depend upon the crystal form. At about $11.0\ \mu$, the $\text{O}-\text{H}$ out-of-plane deformation, no two crystal forms have the same absorption and this region is, therefore, very suitable for identification of a specific polymorph. The spectra of two polymorphic forms of stearic acid are shown in Figure 26.

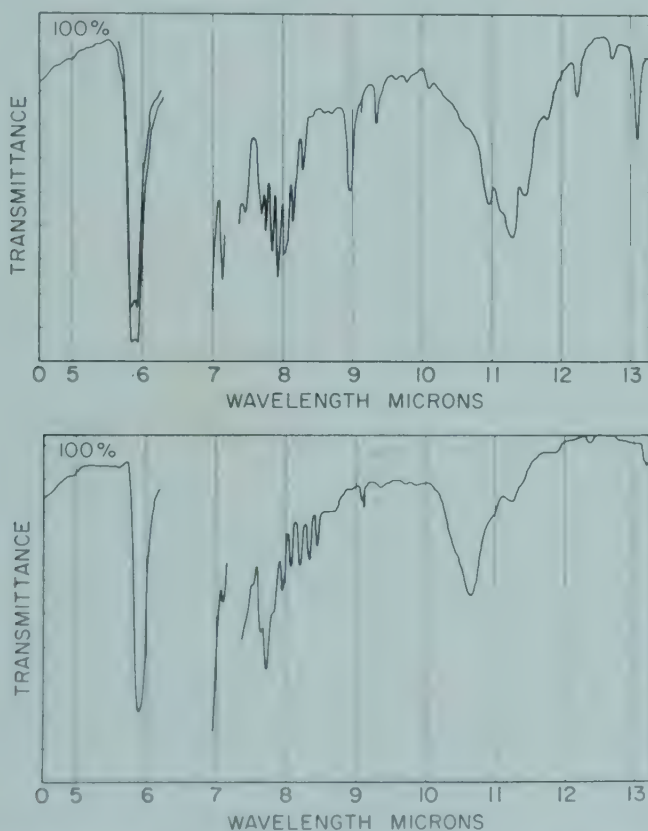


Fig. 26. Infrared spectra of crystalline polymorphic forms of stearic acid (338).

There exists an extensive literature relative to the polymorphic behavior of mono-, di-, and triglycerides. This phenomenon has been investigated largely by means of thermal and x-ray diffraction techniques. Interpretation of the resultant data gave rise to two schools of thought

regarding the number, nature, and nomenclature of the various polymorphic modifications. As was discussed in the preceding chapter, the two schools arose more or less simultaneously in the United States (338a-338c) and in England (338d). After some years it became apparent that the divergent views could not be resolved solely by recourse to thermal and x-ray diffraction measurements.

Between 1955 and 1957 Chapman (339-339c) published several reports in which it was demonstrated that infrared absorption spectra of the crystalline phase could be used to differentiate polymorphic forms of the mono-, di- and triglycerides and to follow polymorphic changes of these materials. From infrared spectra, the α -, sub- α -, β -, and β' -forms of 1-monostearin can readily be distinguished (339a) from one another. In particular, the sub- α -form can easily be differentiated from the β' -form, whereas clear differentiation of these forms is difficult from x-ray powder photographs. By means of infrared curves it can be shown: (a) that the α -form is reasonably stable from its melting point down to the melting point of the sub- α -form; (b) that the sub- α -form has a definite crystalline lattice, contrary to the observations of Malkin (338d), and is quite stable at room temperature; and (c) that the transition of the sub- α - to the α -form is reversible. These observations agree with those derived from x-ray diffraction by Lutton and Jackson (340).

Only one polymorphic form of the 2-monoglycerides was found which agrees with the x-ray data of Daubert and Clarke (341) and of Filer *et al.* (338b) indicating that 2-monoglycerides do not exhibit polymorphism, but which conflicts with the existence of α - and β -modifications postulated by Malkin (338d). The first form to crystallize when liquid 2-monomyristin cools is the stable β -form, identical with that obtained by crystallization from solvents. No evidence for an α -form was observed.

Both the β - and the β' -form were observed in a study of the infrared absorption spectra of 1,3-diglycerides (339b), in agreement with x-ray data of Baur *et al.* (342), but no α -form, as reported by Malkin *et al.* (342a) on the basis of x-ray spectra, was observed. Infrared absorption spectra afford a convenient method for differentiating between the polymorphic β - and β' -forms of 1,3-diglycerides.

Examination of the saturated triglycerides, tripalmitin, tristearin, and trilaurin, revealed three polymorphic forms which could be differentiated by means of their infrared absorption curves (339b). Spectral curves for only two forms of trilaurin were obtainable because the lowest melting form melts below the operating temperature of the spectrophotometer. The infrared data were interpreted as indicating the existence of the α -

β' -, and β -forms described by Lutton (338c) on the basis of x-ray spectra, rather than the vitreous, α -, β' - and β -forms reported by Clarkson and Malkin (342b).

Examination of the infrared spectra of 1-palmitodistearin and 1-stearodipalmitin revealed an α -, β' -, and β -form which could readily be differentiated by means of characteristic absorption bands (339c). These results agree with the x-ray and thermal data of Lutton (338c). Similarly, spectra of 2-palmitodistearin and 2-stearodipalmitin revealed only two polymorphic forms, again in agreement with the results obtained by Lutton, but contrary to the reported observations of Malkin and Meara (342c) that four forms of these glycerides exist. The infrared spectrum of 2-palmitodistearin indicated that the two polymorphic modifications are the α - and β -forms, but the spectrum of 2-stearodipalmitin indicated that the two modifications were the α - and β' -forms. Based on x-ray short spacing values, Lutton *et al.* (342d) had previously designated the two polymorphic modifications of this glyceride as the α - and β' -forms.

The afore-described infrared data of Chapman support the observations and conclusions of the group of American investigators (338a–338c) on the basis of evidence derived from x-ray spectra, rather than those of Malkin (338d) on the basis of association of x-ray data with melting points. Chapman found no evidence for the so-called vitreous form of glycerides described by Malkin, and questioned by the American group of workers. The classification of the polymorphic forms of glycerides proposed by Lutton and its extension to include 1-monoglycerides with the addition of a sub- α -form seems to have been confirmed by Chapman, who concluded "that for the glycerides so far examined, the infrared spectra show Lutton's short-spacing classification to be reasonable and useful and to be based on sub-cell symmetry."

Davison and Cornish (343) compared the infrared absorption curves of amorphous and crystalline polyesters, and Cornish and Davison (344) reported a similar comparison of α,ω -dicarboxylic acid in the crystalline and molten states. The spectra of both groups of compounds exhibited several differences, attributed to approximately planar *trans*-configurations in the crystalline state and continuous random configuration in the amorphous or molten state.

Sufficient data are now available to demonstrate that infrared spectra of the crystalline phase of fatty acids and related compounds, in contrast to the corresponding spectra of the amorphous (molten or solution) phase, can be applied to (1) indicate chain length of unbranched compounds; (2) estimate the degree of bonding of specific groups; and (3) differentiate

polymorphic forms of a compound, and follow polymorphic changes. Future investigations will undoubtedly reveal other practical applications of infrared absorption spectra to the solid state of the aforementioned compounds as well as to other related substances.

(1) Fingerprint Technique

The foregoing discussion of the applications of infrared absorption to fatty acids and their derivatives has been concerned entirely with the "group-frequency" type of analysis, essentially as suggested by Julius (180). Another method of analysis employing infrared absorption spectra is the "fingerprint technique" involving, as the name implies, identification by a direct comparison of the spectrum of an unknown material with a series of standard spectra. The success of this technique depends upon the availability of an extensive library of infrared spectra of pure compounds. This requirement has delayed the development of the fingerprint method of chemical identification and favored the group-frequency type of analysis. The potential advantages of identification of any molecule by a simple comparison of its infrared absorption spectrum are so great that a number of organizations have combined their efforts to obtain and maintain a fingerprint file of as many known molecules as possible with the eventual hope of including every known compound and molecular form thereof.

Anticipation that a wholly adequate file of infrared spectra will eventually become available requires a solution of the problem of selecting from this file a particular spectrum required for comparison. This problem has received considerable attention, and progress is being made toward its solution. The American Society of Testing Materials has made available infrared absorption data, not as infrared spectral curves three or four feet long, but in the form of IBM cards on which all the specific characteristic absorption data, as well as certain pertinent chemical data, have been coded for a given compound. An infrared fingerprint identification is made with the aid of an IBM-sorter which rapidly rejects cards which do not have a required absorption maximum, an observed region of transparency, or a particular atom.

In 1955 Otis *et al.* (345) described the use of combinations of the above-mentioned factors in a simultaneous multiple sorting which greatly speeds up this part of the identification. About 20,000 cards are available and additional ones are being processed. An intensive program under the auspices of the ASTM is being pursued to increase the number of available

infrared-spectra fingerprints of pure compounds. A considerable portion of the data being coded is from private collections of research institutions and industrial firms. These data, because of reluctance of editors of most technical journals to publish large numbers of infrared curves, have never appeared, and probably never will appear in the published literature. This service provides, therefore, considerable additional data to that which can be obtained through library searches. Once a library of cards is established, qualitative chemical analysis consists merely in obtaining an infrared absorption spectrum of the unknown compound, and selecting the comparison card or cards with the aid of an IBM sorting machine. If the determined spectrum is that of a new and heretofore unknown compound, elucidation of its structure can be aided by comparing the determined spectrum with those selected spectra which exhibit similar or identical bands in various portions of the spectrum. This technique is being used in many laboratories but, to the author's knowledge, it has not been used in fatty acid chemistry, despite its applicability to the analysis of fatty acids and their derivatives.

(m) Near Infrared

The earliest applications of infrared absorption spectra to problems of chemical analysis and to elucidation of molecular structure were confined to those spectral regions which could be detected by means of the photographic plate. Dependency upon the photographic plate limited measurements to the near infrared, i.e., the region just beyond the visible red or to not more than $3\ \mu$. The introduction of thermocouples and ballometers as detectors made possible the use of rock salt optics, and thereafter almost all published infrared spectra, including those discussed in this chapter, have been in the region of 2 to $15\ \mu$, which is transparent to sodium chloride. Improvements in automatic recording quartz spectrophotometers, as exemplified in the Model 14 Cary Spectrophotometer, for measuring ultraviolet and visible spectra have extended the range of these instruments to about $3\ \mu$, thus making it possible to measure near infrared spectra easily, rapidly, accurately, and with the satisfactory resolution afforded by quartz optics. The potential utility of near infrared spectra to problems of fatty acid chemistry are only now being explored.

Kaye (345a) published a comprehensive review of near infrared spectroscopy and described an infrared spectrophotometer (Model DK-2 Beckman Spectrophotometer) redesigned to include the near infrared region. Although the article is not written with the specific viewpoint of

the fatty acid chemist in mind, it nevertheless contains considerable data and information with reference to techniques, band correlations, applications, and limitations of this region of the spectra which are of value and interest to the specialist in the field of fatty acids.

The near infrared region has been investigated by several workers for the quantitative determination of *cis* unsaturation. *Cis* bands which occur in the $10\ \mu$ region (where analyses for *trans* isomer content have been very satisfactory) have been shown to be inadequate for diagnostic purposes. The near infrared, on the other hand, is characterized by the absence of absorption bands which can be attributed to *trans* isomers. Thus in this region *cis* bands can be accurately measured in the presence of both *trans*-unsaturated and saturated components.

Holman and Edmondson (345b) published a survey of the near infrared spectra of 63 fatty acids and related substances. They found that *cis*-unsaturated compounds exhibit bands at 2.15 and $2.19\ \mu$. These bands are specific for isolated *cis*-bonds and are not observed in the spectra of saturated compounds, *trans*-unsaturated compounds or conjugated *cis*-unsaturated compounds. They offer a method for the measurement of *cis*-isomers having isolated double bonds, analogous to the determination of *trans*-unsaturation from measurements in the band at $10.36\ \mu$. Bands associated with conjugated double bonds, triple bonds, carboxyl, hydroxyl and carbonyl groups, and with amines and esters were discussed by Holman and Edmondson and suggestions were made concerning their applications to fatty acid chemistry.

Holman, Ener, and Edmondson (345c) investigated the application of near infrared absorption to the analysis of fatty acids and fatty acid derivatives for *cis* isomer content. They reported that the method could be employed for rapid analysis of fatty acids, methyl and ethyl esters, triglycerides, cholesteryl esters, and fatty aldehydes. They compared results for the analysis of these types of materials for *cis* content by the direct near infrared procedure with the calculation by means of a determination of *trans* isomer content (from measurements in the $10\ \mu$ region), estimation of total unsaturation by means of iodine value, and evaluation of *cis* isomer by difference. Results by the direct and indirect methods were in reasonably good agreement.

Goddu (345d) showed that *cis* double bonds could be determined quantitatively at $2.1\ \mu$ with a sensitivity of about 1% $-\text{CH}=\text{CH}-$ and that at 1.6 and $2.1\ \mu$ terminal double bonds in several types of organic molecules could be estimated with a sensitivity within 0.01% $-\text{C}=\text{CH}_2$.

A detailed procedure for the determination of *cis* unsaturation in vege-

table and animal oils and fats by near infrared spectroscopy has been described by Fenton and Crisler (345e). They reported details for the satisfactory application of the method to the analysis of vegetable and drying oils, hydrogenated oils, shortenings, and margarines by a differential technique.

Results of these investigators have shown that the near infrared procedure has several advantages for the determination of *cis* isomer content as it is direct, rapid, selective, simple, and sensitive. It will undoubtedly be added to the growing list of procedures which are becoming routine tools of considerable help to the lipid chemist.

Another application of the near infrared spectroscopy, which may be of even greater interest to the fatty acid chemist, is the direct determination of hydroxyl number by measurement of the —O—H overtone band at about $1.4\ \mu$. Crisler and Burrill (345f) have described a method for the determination of hydroxyl value of aliphatic primary alcohols from measurement of the hydroxyl-stretching overtone band at $1.4\ \mu$. Comparisons of the near-infrared and chemical acetic anhydride—pyridine methods showed better agreement, standard deviation 0.27, than did tests of the precision of the chemical method alone, standard deviation 0.77, for hydroxyl value determinations in the same range. These authors also showed that there is a wide range of values of absorptivities for the various types of alcohols and that a single calibration curve cannot be used for the determination of hydroxyl values of primary, secondary, tertiary, branch alcohols and phenolic compounds, etc. The near-infrared procedure can be used, however, for any —O—H containing system once a suitable calibration curve for the particular type of system has been obtained.

Interferences from acids, alcohols, hydroperoxides and other —O—H containing compounds and from amides, amines and oxiamines were corrected for mathematically in a method described by C. L. Hilton (345g) using near-infrared bands between 2.0 and $3.0\ \mu$ to determine the hydroxyl number of polyesters and polyethers.

The applications of near infrared spectroscopy to the examination of autoxidation products of fats have been described by Slover and Dugan (345h). They observed that hydroperoxides, alcohols, esters, aldehydes, and ketones absorb in the narrow spectral range from 2.7 to $3.0\ \mu$. Alcohols may be distinguished from hydroperoxides and acids, but the absorption peaks of the two last-mentioned compounds are too close to each other to be resolved. In autoxidizing methyl oleate the increase in alcohol, carbonyl, and combined acid-hydroperoxide can be followed

in the near infrared spectra. In the absence of acid, the increase in the hydroperoxide absorption is linear with peroxide value.

Holman and coworkers (345i) found that only those compounds having an —O—O—H group exhibited absorption bands at 1.46 and 2.07 μ . They used these bands to follow the thermal decomposition of methyl oleate hydroperoxide and the autoxidation of methyl linoleate. Intensities of the bands at 1.46 and 2.07 μ were shown, in both studies, to parallel the iodometric peroxide values.

Terminal epoxides were shown to have sharp absorption bands at about 1.65 and 2.20 μ by Goddu and Delker (345j) who used these bands for the quantitative determination of the epoxide ring in the range of 10 gamma per ml. of C—CH_2 . They demonstrated an accuracy and precision in this range of from ± 1 to 2% of the amount present.

6. Microwave Spectroscopy

(a) Introduction

Beyond the infrared, and overlapping it somewhat, is the microwave region of the electromagnetic spectrum (Fig. 14), loosely defined as extending from 1 mm., i.e., the edge of the long infrared, to 1000 mm., the beginning of radio frequency region. From the quantum equation, $\Delta E = h\nu$, it may be determined that at these shorter frequencies changes of energy are relatively small. It was pointed out in earlier sections of this chapter that x-ray spectra arise from electronic transitions between the inner shells, i.e., the kernels of the atoms; that electronic spectra arise from electronic transitions between the outer or valence electrons; and that infrared spectra arise from vibrational and rotational changes within a single electronic level. These three types of transitions involve increasingly smaller changes in energy. Microwave spectra, which are accompanied by still smaller changes of energy, arise from changes in rotational levels within a single vibrational level, i.e., microwave spectra are mainly pure rotational spectra.

Besides differentiations based on type or degree of changes in energy, microwave spectra are distinguished from optical spectra by basically different methods of generating, detecting, and measuring the radiation. The source of microwaves is usually an electronic tube, which emits radiation through a hollow metal pipe, called a waveguide. The microwaves are detected after passage through a region of low-pressure gas (10 mm. to 10^{-4} mm. Hg) by a silicon "crystal" or other detecting device.

This detector produces an electrical signal which is proportional to the power of the microwave and which, after amplification, is observed on a meter or oscilloscope. As the frequency of the microwaves is varied, absorption appears as a sudden decrease in the voltage output of the detector.

Applications of microwave spectroscopy are confined to absorption spectra. Emission lines, commonly employed in the visible and ultra-violet regions, as previously illustrated, decrease very rapidly in intensity with decrease in frequency, and are much too weak for detection at microwave frequencies. For this reason, as in the case of emission in the infrared region, emission in the microwave region is not particularly useful for analytical purposes.

At gas pressures of the order of one atmosphere, a small microwave absorption may occur over a wide range of frequencies. As the pressure is lowered, the range of frequencies absorbed decreases proportionally down to pressures near 10^{-3} mm. of mercury. At these pressures the range is so small that the term "absorption line" is commonly used. It must be kept in mind, however, that microwave absorption is a molecular process and that the term "characteristic microwave absorption line" of a specific molecule is a result of experimental measurement at low pressures where the width of the band is so small that a line is suggested. These narrow absorption bands are probably the most important feature of microwave spectroscopy for qualitative analysis.

(b) Qualitative Analysis

There are two principal disadvantages or limitations to microwave spectroscopy, namely, (1) it is limited to gaseous substances, and (2) it is limited to gases having a dipole moment. Certain types of characteristic microwave absorption are exhibited by liquids or solids, such as paramagnetic absorptions, but they have only very specialized uses and, for purposes of chemical analysis, microwave spectra are practically restricted to gases. This restriction is not, however, as great as might at first be assumed. The substance to be analyzed need have a vapor pressure of not more than about 10^{-3} mm. of mercury at some obtainable temperature. Microwave spectrometers can now be operated at temperatures up to 1000° K. (726.8° C.); hence attainment of the required vapor pressure is not a serious limitation except for the numerous molecules which dissociate when vaporized at high temperatures. The requirement that the gas must have a dipole moment eliminates all symmetrical molecules.

Carbon dioxide, nitrogen, and benzene exhibit no microwave absorption.

Microwave analysis, in practically all instances, involves the detection and measurement of pure rotational lines. The positions of these lines depend only upon the principal moments of inertia of the molecule as a whole. Microwave spectra, therefore, unlike infrared spectra, cannot be used to identify component groups within a given molecule, but only to identify the molecule as a whole. Microwave analysis is presently limited to rather simple molecules, but conceivably it can be developed to provide rapid and positive identification for a large number of organic compounds.

One advantage of the use of microwave spectra in place of infrared absorption spectra for qualitative identification is that the high resolution of the former makes identification considerably more certain. The microwave region from 1 to 3 mm. covers a span of 2,000,000 megacycles. If lines 1000 kilocycles apart can be separated and identified, there are 2,000,000 spectral spaces available in this range alone, more than in the remainder of the microwave region beyond 3 mm. to the edge of the radio frequency region. Gordy (346) has made a comparison of this available region with that of the infrared for identification of molecules. Assuming that an average resolution of 1 cm^{-1} is obtainable over the entire infrared region, he calculated that only 10,000 spectral spaces are available in this region. Above about 3 mm. the microwave region suffers from underpopulation. Below 1 mm. the infrared region suffers from overpopulation of detectable lines. The optimum region for qualitative identification appears to lie in the region of 1 to 3 mm. of the microwave spectra. Qualitative analysis of many substances with a vapor pressure of about 10^{-3} mm. of mercury at an obtainable temperature can be made simply, directly, rapidly, and with a high degree of certainty by the use of microwave spectroscopy. With the high resolution obtainable, there is little possibility of overlapping of lines or confusion in identifying them.

Qualitative identifications can be made by measuring frequencies of observed absorption lines and comparing them with tabulations of known microwave lines of pure substances. Tabulation of microwave lines prepared by Kisliuk and Townes (347) includes 1800 lines of 92 different substances whose microwave spectra were known up to 1950. If, in the narrow region 20,000 to 30,000 megacycles, each of 100 substances in a gas mixture has 20 lines, there is less than one chance in 10^6 that more than one-third of the lines of some one of the substances will be overlapped by lines of another substance. Thus, if the microwave lines are sufficiently intense, each of a large number of substances can be identified in a single gas mixture. This situation is very different from that existing

in the infrared region, where the rotation-vibration bands of a substance may give lines separated by less than the resolving power of the infrared spectrophotometer—in which case, the spectrum of the substance becomes a series of continuous bands and interferences between the spectra of two or more substances may be very troublesome.

Another advantage of microwave spectroscopy is the rather small amount of gas required to detect absorption. A typical microwave cell has a volume of a few hundred cubic centimeters and is filled to a pressure of about 10^{-3} mm. of mercury. This corresponds roughly to about 10^{-7} moles of gas or a few micrograms of material. If the gas has very strong lines, an amount of gas 10^5 times smaller, or about 10^{-12} , is sufficient for detection. Thus, the small quantity of gas needed, makes analysis by microwave spectroscopy practical in microchemical investigations.

Microwave spectroscopy has not been used for the identification of fatty acids or their derivatives. Within the limits of the method some substances could be detected. Once a sufficiently complete tabulation of the microwave lines of pure fatty acids and their derivatives has been compiled, the advantages of using microwave spectra in the region of 1 to 3 mm. for the rapid and positive identification of substances, particularly of components in complex mixtures, should not be overlooked. However, as previously mentioned, microwave spectroscopy is limited to rather simple molecules. The sensitivity of microwave spectra to very small changes within the molecule proscribes the application of this form of spectroscopy to molecules having a large number of atoms. For example, a molecule with 25 atoms has approximately 70 modes of internal vibration, many of which may be excited at ordinary temperatures to split each rotational line into as many different frequencies. If each rotational line is split into multiplets, each component is so weak that detection may be difficult and it is therefore doubtful that microwave spectroscopy could be successfully applied with molecules having much more than about 25 atoms.

(c) Quantitative Analysis

Measurement of absolute intensities in microwave spectroscopy are difficult to make and, in fact, are not required for quantitative determinations. A quantitative determination can be made by:

(a) Measuring the maximum of a selected absorption line and, taking this measurement as proportional to the fractional abundance of the particular component whose absorption line is being measured. The accuracy

of the result depends on the reliability of the assumption that absorption at the maximum of the band is proportional to fractional abundance.

(b) Considering the fact that the line-width parameter, $\Delta\nu$, is somewhat dependent on the composition of the gas and that the fractional abundance is strictly proportional, not to the maximum absorption, but to this value multiplied by the ratio $\Delta\nu/P$, then the measurement of these terms affords a precise determination. This operation is somewhat comparable to an integrated absorption measurement in infrared absorption spectroscopy.

(c) Comparing the maximum of absorption for the unknown sample with values from known mixtures which are similar to it in composition. The use of this method with standard mixtures of known compounds appears to be the simplest and often the most reliable microwave spectroscopic technique, because quantitative analyses made by this form of spectroscopy are made after the components in the mixtures have been qualitatively identified.

It is probable that the limitations imposed by molecular size will prevent widespread application of microwave spectra in the field of high molecular weight fatty acids and their derivatives, although there may be some specific case where conceivably it might be employed to advantage. The interested reader will find detailed descriptions of the theory, apparatus, and applications of microwave spectroscopy in the monograph of Gordy *et al.* (11) and in the less extensive reviews of Gordy (346), Coles (348), and Bak (349). Applications of microwave spectroscopy to chemical analyses will be found in the publications of Dailey (350), Hughes (351), and Southern *et al.* (352).

7. Nuclear Magnetic Resonance

In the preceding sections, applications of spectra arising from various types of transitions of electrons within the atom or molecule were discussed. They included electron transitions within the kernel which give rise to x-ray spectra; transitions of valence electrons which give rise to electronic emission and absorption in the visible and ultraviolet regions of the electromagnetic spectrum; and transitions involving small energy changes which give rise to vibrational-rotational spectra in the infrared region. In the last section there were discussed changes in rotation levels within a single vibrational level which give rise to microwave spectra. Although the entire electromagnetic spectrum was considered in the preceding sections, these considerations do not exhaust the limits of spectroscopy. Transitions of electrons between various energy levels about

the nucleus account for all x-ray and optical spectra. These spectra could be accounted for even if the nucleus were considered to be a solid core.

The nuclei are by no means simple systems. They are composed of several particles, termed nucleons, of which the most important are the proton with a mass two thousand times larger than that of the electron and carrying a positive electrical charge; and the neutron with a mass almost equal to the mass of the proton, but electrically neutral, i.e., without a charge. These particles, like electrons, must be considered as having rapid motion within narrow limits of space. Changes in energy levels of these moving particles can also give rise to spectra.

Many aspects of the motion of nucleons are still in need of investigation, but one fact is well established, namely, that irrespective of the paths followed by the individual nucleons, in about half of the known nuclei there exists a rotation of the nucleus as a whole about an axis which passes through its center of gravity.

Ampère demonstrated experimentally that a loop of wire carrying an electric current exerts at a distance the same forces of attraction as a magnet. Electrons rotating in their respective shells are essentially current. This analogy has been used to explain the magnetic properties of atoms and molecules. The rotation of charged particles within the nucleus, similar to the circulation of the electrons in the atom, is also equivalent to an Amperian current so that nuclei should be expected to exhibit the properties of elementary magnets.

The strength of a magnet is measured by its "magnetic moment" which is defined as the pole strength of the north and south poles multiplied by their separation. In the case of an atom and a nucleus with the same angular momentum, their magnetic moments should be in the approximate inverse ratio of their respective masses, and it is a demonstrated fact that the magnetic moment of a spinning nucleus is about a thousand times smaller than that of an atom.

The fact that the magnets of nuclei are very much weaker than atomic magnets necessitates the use of a different technique to study them. If we consider the spinning nuclei in a magnetic field, the miniature magnets will be oriented in the direction of the axis of rotation. The north poles of these tiny magnets will be repelled by a downward force from the north pole of the magnetic field and upward by an opposite and equal force by repulsion of their south poles by the south pole of the magnetic field. The spinning nucleus may be assumed to resemble a spinning top in which the two opposite and equal forces are the downward force provided by the

weight of the top, and the upward or opposing force exerted by and at the point of contact with its support.

Observation of a spinning top reveals that it performs a slow rotation around the vertical which is distinguishable from the rotation around its axis. The former rotation is called a precession. By analogy, it would be expected that the axis of the spinning nucleus, and hence its magnetic moment, would perform a similar precession. The rate at which this precession occurs is proportional to the strength of the magnet. The factor of proportionality is given by a quantity called the "gyromagnetic ratio" which is defined as the ratio of the magnetic moment to the angular momentum of the nucleus. The frequency of this precession is much lower than that of the motion of the nucleons within the nucleus. That the frequency of this precession lies in the range of radio frequencies is significant and fortunate, because in this range electrical effects of extremely small magnitudes can be amplified and measured with very high accuracy through the application of present-day electronics.

Whenever the polarization of the nuclei-magnets is oriented parallel to the magnetic field, there is no detectable effect because the precession occurs with zero angle and therefore the direction of the polarization remains unchanged. If, however, an oscillating field is placed perpendicular to the magnetic field, and if the frequency of this oscillating field is made equal to that of the nuclear precession, "magnetic resonance" will occur and will result in a tilting of the nuclear polarization with respect to the magnetic field. The nuclear polarization, tilted against the magnetic field and performing a precession around the direction of this field, is analogous to the change of magnetic flux with a coil of wire. According to the principle of electromagnetic induction such motion would produce a voltage differential between the terminals of the coil of wire. To reproduce this effect it is merely necessary to wind a few turns of wire around the sample of material whose nuclear magnetic resonance spectrum it is desired to investigate. Such a wire is called the "receiver coil" to distinguish it from the "transmitter coil" used to produce the oscillating field at right angles to the magnetic field.

The precession of the tilted polarization induces an alternating voltage of the same frequency between the terminals of the "receiver coil." This potential difference can be used to produce a weak current which can be amplified and measured with extreme accuracy. The electrical signal can be traced out by a cathode-ray tube or the amplified current can be made to drive a pen on a recording potentiometer. If the field strength is changing continuously, a trace with peaks, in which the frequency of

precession of the nucleus is equal to the frequency of the applied oscillating field, will be seen on the cathode-ray tube or traced on the recorder chart. The vertical displacement measures the magnitude of the signal and the horizontal displacement is proportional to the strength of the magnetic field. In this manner a nuclear magnetic spectrum is produced.

When nuclear magnetic moments are aligned in a magnetic field and thermal equilibrium is reached, the nuclei are distributed according to a Boltzmann distribution law which states that,

$$N_m/N_{m-1} = e^{\Delta W/kT}$$

where W is the energy of the transition between the Zeeman levels m and $m - 1$, N_m and N_{m-1} are the populations of the two levels, k is the Boltzmann gas constant and T is the absolute temperature. The energy of each Zeeman level is the work done in aligning the magnetic moment with the field. Nuclear magnetic resonance spectroscopy involves transitions between the Zeeman levels of an atomic nucleus whose magnetic moment is interacting with an applied magnetic field. The afore-described phenomenon represents an additional type of energy-level transition, and the process properly belongs to the realm of spectroscopy.

As a nuclear magnetic resonance spectrum is being traced with continually changing applied field strengths, there will occur perturbations of the magnetic field at the position of the nucleus caused by the motions of the surrounding electrons. Depending upon the particular chemical compound or group in which the resonance is occurring, there may be found several closely spaced peaks, especially if several non-equivalent structural features are present in material under observation.

The study of such chemical shifts is called high-resolution nuclear magnetic resonance spectroscopy, and constitutes a phase of nuclear magnetism of major interest for analysis and identification. For the measurement of some peaks, high resolution is required. To control the breadths of the nuclear magnetic resonances, the homogeneity of the magnetic field in which the sample is placed is most important. Rigid requirements of homogeneity must be met in order to apply high-resolution nuclear magnetic spectroscopy. Magnets can be manufactured with fields which do not vary more than one part in one hundred thousand over a region several inches in diameter. For high-resolution nuclear magnetic resonance spectroscopy, the size of the sample is reduced until its homogeneity is of the order of one part in ten million or one part in one hundred million. Even with such homogeneity, Bloch (353) and Anderson and Arnold (354) have shown that spinning the sample rapidly can level out

inhomogeneities in the magnetic field over a sample and produce high-resolution nuclear magnetic resonance spectra with enhanced sharpness of its peaks.

Bloch (355) used ethyl alcohol to illustrate the potentialities of nuclear magnetic resonance spectra. The spectrum of this compound, at sufficiently high resolution, exhibits three peaks originating from proton signals, instead of one which is found in the spectrum of water. These three peaks have been shown to arise from the protons in the chemical groups $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{OH}$. The areas under the peaks are in the ratio 3:2:1, corresponding to the number of hydrogen atoms contained in each group. High-resolution nuclear magnetic resonance spectra has "confirmed" the chemists concept of the structure of ethyl alcohol. The application of such measurements and principles to organic compounds including fatty acids and their derivatives, offers a new and potentially powerful tool for the elucidation of structure, for qualitative identification, and for quantitative determination of such compounds.

Advances in nuclear magnetic resonance spectroscopy, especially in stability and resolution, now permit differentiation of organic substances that differ only in the position of a hydrogen atom.

In Figure 27 there is reproduced (356) the high-resolution nuclear

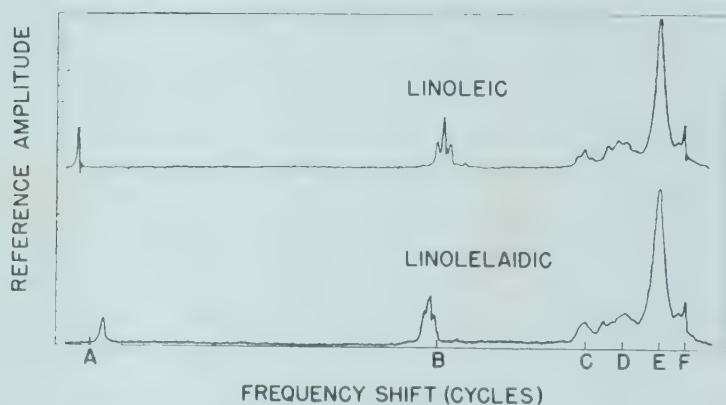


Fig. 27. Nuclear magnetic resonance spectra of linoleic and linolelaidic acids (Courtesy J. N. Shoolery (357) and J. E. Callan).

magnetic resonance spectra of linoleic and linolelaidic (*cis,cis*-9,12- and *trans,trans*-9,12-octadecadienoic) acids. The peaks represent the protons with different types of chemical bondings and the area below each peak reflects the number of protons in each type of chemical bonding.

In Figure 27, the peak designated:

"A" corresponds to the carboxyl proton and the area below it represents one hydrogen atom;

"B" represents four CH= protons and should have an area four times larger than "A";

"C" represents the central methylene group corresponding to the eleventh carbon atom of the chain;

"D" represents the three CH_2 groups corresponding to C_2 , C_8 , and C_{14} ;

"E" represents all the other CH_2 groups; and

"F" is a reflection of the terminal CH_3 group.

The main difference in the two spectra in Figure 27 is that linoleic acid (*cis,cis*) exhibits a stronger coupling of the spins of the CH= protons at C_9 , C_{10} , C_{12} , and C_{13} to the spins of the adjacent methylene groups than does linolelaidic (*trans,trans*) acid. The triplet peak, "B," in linoleic acid is more widely split than the corresponding peak in linolelaidic acid. The central CH_2 in the latter acid may be coupled not only to the adjacent CH= protons, but also more weakly through the double bond to the C= protons at the C_9 and C_{13} positions. Spin-coupling differences have been noted in smaller molecules in which such groups are *cis* and *trans* to one another (357).

The important deduction which can be made from Figure 27 is that the two acids can be readily distinguished and identified by high-resolution nuclear magnetic resonance spectra and that specific groups can be identified and estimated quantitatively.

Nuclear magnetic resonance appears to offer almost unlimited opportunity for the study of the structure of organic molecules. Studies of the proton spin of H^1 are applicable to almost all organic molecules, but nuclear magnetic resonance investigations are by no means limited to H^1 . Among the growing number of nuclei which have been investigated are F^{19} , P^{31} , Si^{29} , and B^{11} . The potential applications of high-resolution nuclear magnetic resonance spectroscopy to problems of the elucidation of structure of fatty acids, their derivatives, and related compounds to the differentiation of geometrical isomers and for the positive identification of specific compounds appear almost endless.

For additional information relative to the discovery, theory, and applications of nuclear magnetic resonance, the reader is referred to the publications of Bloch (355,358) and Purcell (359,360), and also to that of Shoolery (361); this latter publication is concerned with the application of nuclear magnetic resonance to analytical chemistry. A series of technical bulletins published by Varian Associates (362), pioneers in the instrumentation of nuclear magnetic resonance equipment, affords an ex-

cellent introduction to the instrumentation and application of nuclear magnetic resonance spectroscopy.

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CHAPTER VI
PROPERTIES OF THE LIQUID STATE

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New Orleans, Louisiana

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1. Introduction

The utility and applicability of a given substance is determined by its physical properties and, more often than not, by the relative value of one specific property as compared to that of other members of the same class of compounds. For example, the sodium salts of lauric, myristic, and palmitic acids find extensive employment as components of soaps because, of all the saturated fatty acids, they possess solubilities and surface-acting properties which render them most valuable as detergents. Similarly, castor oil and ricinoleic acid find many uses in the textile, petroleum, and lubrication fields because they exhibit certain viscosity behavior and surface-acting properties not found in other vegetable oils and fatty acids.

Generally speaking, as our knowledge of the physical properties of a given material increases, the applications and uses of this material likewise increase. For a long time, man had to rely almost entirely on his perceptive senses as a means of determining the nature and estimating the magnitude of the properties of matter and, consequently, such knowledge as was obtained was purely qualitative. Gradually one means after another has been devised to measure various specific properties. These devices in their original forms were relatively simple and not highly accurate, as, for example, the chemical balance, the thermometer, and simple lenses, but with the development of more complicated and precise instruments, many new and sometimes quite abstract properties were discovered and measured with an increasing degree of accuracy. Many of these have proved to be extremely valuable both from a theoretical as well as a practical point of view.

Many organic, and especially synthetic organic, compounds have been systematically investigated with respect to a variety of physical properties, and data pertaining to them have been compiled, classified, and recorded in readily available form. This, however, has not been the case with regard to the naturally occurring higher fatty acids despite the fact that some of them have been known and have been the subject of scientific investigation for a century or more. Until recently, such measurements as have been made were often carried out in an unsystematic manner and at times on not very pure materials. Many of the measurements which have been reported are so scattered throughout a voluminous literature that they are located only by chance, or by the expenditure of a disproportionate amount of time and energy.

In this chapter there are brought together considerable data with reference to a number of the more important properties of the fatty acids.

pure mono-, di-, and triglycerides, and some of their derivatives. In addition to colligative properties, fatty acids possess other properties which are not only of theoretical interest but also of considerable practical importance. These properties, which are of particular importance in the liquid state, include density, molar volume, viscosity, surface tension, refractivity, etc. They are dependent upon the kind, number, or position of atoms in the molecule, and upon the attractive or repulsive forces which one molecule exerts on another. This is true also of some of the other properties, such as optical rotation, melting point, etc.

An effort has been made to present these data in a critical manner but this has not always been possible, as in some cases only a single measurement of a given property has been reported. In other cases there is no way of judging the purity of the material used, or the accuracy of the method employed, in measuring a specific property. Many gaps occur in the data for some of the homologous series, and it is not always possible to determine the approximate value of the undetermined property by interpolation of such data as are available.

2. Heats of Formation and Combustion

(a) *Saturated Acids*

Practically all of the available information on the heats of formation and combustion of the higher fatty acids and their derivatives is due to Stohmann and co-workers (1,2). These investigations are now nearly seventy years old and were carried out with products of unknown purity.

Kharasch (3) critically reviewed the literature on the heats of combustion of organic compounds and compiled a table of "best" values available up to 1929. This table includes a considerable number of saturated, unsaturated, mono- and polybasic, hydroxy, keto and other substituted aliphatic acids. The table also includes, in many cases, calculated values for heats of combustion and the experimentally determined values most nearly in agreement with the calculated value. Because of this selection, a much higher degree of correspondence is indicated between the experimental and determined values than would otherwise be expected on the basis of the probable purity of the acids generally available at the time many of the measurements were made. This is especially true of the unsaturated acids which have only been available in a relatively high state of purity since about 1940. No unsaturated acid containing more than one double or one triple bond is included in the table.

The heats of combustion in Kharasch's table are expressed both in

absolute kilojoules (at constant pressure) per gram molecular weight of substance *in vacuo* and in kilocalories at 15°C. A selected group of compounds from this table are included in a compilation contained in the *International Critical Tables* (4), but the heats of combustion are expressed in 1922 International Combustion Calories per gram formula weight (*in vacuo*) in the liquid state, when combustion is carried out at constant pressure of one atmosphere and at 18–20°C. to form gaseous carbon dioxide and liquid water. The heats of combustion for the saturated fatty acids, and for some branched and polybasic acids from these two compilations are compared in Table 64. Heats of combustion of only

TABLE 64
Heats of Combustion of Saturated Normal,
Branched, and Polybasic Fatty Acids in Kcal.¹⁵^a

Acid	International critical tables (4)	Kharasch (3)	
		Experimental ^b	Calculated
Formic	62.8	62.8	65.1
Acetic	209.4	209.4	208.4
Propionic	365	367.2	364.7
<i>n</i> -Butyric	520	524.3	521.0
Isobutyric		517.4	521.0
<i>n</i> -Valeric	679	681.6	766.3
Caproic	831.0	831.0	833.6
Heptanoic	986.1	986.1	989.9
Capric	1453 (s)	1458.1	1458.8
Undecanoic	1610 (s)	1615.9	1615.1
Lauric	1772 (s)	1771.7	1771.4
Myristic	2086 (s)	2085.8	2084.0
Palmitic	2380 (s)	2398.4	2396.6
Stearic	2698 (s)	2711.8	2709.2
Arachidic	3010 (s)	3025.9	3021.8
Behenic	3338 (s)	3338.4	3334.4
Adipic		668.6 (s)	677.3
Dimethyladipic		986.7 (s)	989.9
Sebacic		1296.4 (s)	1302.5

^a All values for liquid state except where indicated by (s), which indicates solid state.

^b Selected experimental value nearest to calculated.

a few aliphatic esters are found in either of the above-mentioned compilations, and those of Kharasch (3), which are the most extensive, are given in Table 65.

Hancock and co-workers (5) determined the heats of combustion of the

TABLE 65
Heats of Combustion (3) of Fatty Acid Esters Expressed in Kcal.₁₅^o^a

Acid	Methyl ester		Ethyl ester		Triglyceryl ester
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
Formic	233.1		391.7		
Acetic	381.2	381.2	539.7		
Propionic	552.3 (v)	537.5	690.8	693.8	
Fumaric	664.3	671.3			
Butyric	692.8	693.8	851.2	850.1	1941.1
Isobutyric	694.2	693.8	845.7	850.1	
Valeric			1017.5	1006.4	2308.6
Adipic	1019.6	1023.0			
Lauric					5706.3 (s)
Myristic					6650.3 (s)
Erucic					10264.7 (s)

^a All values for liquid state except where indicated by (s), which indicates the solid state, and (v), which indicates the vapor state.

five-carbon fatty acid isomers which exhibit α -branching, and of the methyl and ethyl esters of these acids. From the experimental heat of combustion, the heat of combustion at constant pressure and the heat of formation (at 25°C. and 1 atmosphere) were calculated, using a calorie defined as 4.1840 absolute joules. These results are given in Table 66.

TABLE 66
Heats of Combustion of Isomeric Branched Fatty Acids, and Esters (5)

Material	Heat of combustion			Heat of formation, kcal./mole
	Exptl., cal./g.	Calcd. at constant pressure, kcal./mole		
Valeric acid	6664 $\pm$ 7	681		131
α -Methyl butyric acid	6645 $\pm$ 12	679		133
Isovaleric acid	6629 $\pm$ 8	678		134
Pivalic acid	6622 $\pm$ 5	677 ^a		135
Methyl valerate	7294 $\pm$ 15	848		126
Methyl α -methyl butyrate	7280 $\pm$ 5	846		128
Methyl isovalerate	7271 $\pm$ 5	845		129
Methyl pivalate	7243 $\pm$ 15	842		132
Ethyl valerate	7706 $\pm$ 9	1004		132
Ethyl α -methyl butyrate	7682 $\pm$ 4	1001		135
Ethyl isovalerate	7674 $\pm$ 5	1000		136
Ethyl pivalate	7663 $\pm$ 6	999		138

^a Solid; all others liquid.

The theoretical heats of combustion are 719 for valeric through pivalic acids; 888 for the respective methyl esters; and 1045 for the respective ethyl esters.

(b) *Unsaturated Acids*

Data relative to the long-chain unsaturated fatty acids are likewise nonextensive, as is indicated by reference to Tables 67 and 68 containing

TABLE 67
Comparative Heats of Combustion of Some Saturated and
Unsaturated Fatty Acids, Kcal._{15°}

Acid	Formula	Experi- mental (solid)	Calculated (liquid)	Number of double bonds
Hendecanoic	C ₁₁ H ₂₂ O ₂	1615.9	1615.1	0
Hendecenoic	C ₁₁ H ₂₀ O ₂	1579.7	1576.0	1
Hendecynoic	C ₁₁ H ₁₈ O ₂	1537.8	1544.0	1 triple bond
Stearic	C ₁₈ H ₃₆ O ₂	2711.8	2709.2	0
Oleic (<i>cis</i>)	C ₁₈ H ₃₄ O ₂	2681.8 2657.0	2663.6	1
Elaidic (<i>trans</i>)	C ₁₈ H ₃₄ O ₂	2664.2	2670.1	1
Stearolic	C ₁₈ H ₃₂ O ₂	2628.6	2638.1	1 triple bond
Behenic	C ₂₂ H ₄₄ O ₂	3338.4	3334.4	0
Erucic (<i>cis</i>)	C ₂₂ H ₄₂ O ₂	3296.7	3295.3	1
Brassidic (<i>trans</i>)	C ₂₂ H ₄₂ O ₂	3290.1	3288.8	1
Behenolic	C ₂₂ H ₄₀ O ₂	3254.9	3263.3	1 triple bond

TABLE 68
Differences in Heats of Combustion in Kcal._{15°} for Pairs
of Acids Shown in Table 67

Pairs of acids	Experimental	Calculated
Hendecanoic-hendecenoic	36.2	39.1
Hendecanoic-hendecynoic	78.1	71.1
Stearic-oleic	30.0 and 54.8	45.6
Stearic-stearolic	83.2	71.1
Behenic-erucic	41.7	39.1
Behenic-behenolic	83.5	71.1
Oleic-elaidic	17.6 and -7.2	-6.5
Erucic-brassidic	6.6	6.5

the values for the heats of combustion of several saturated acids, the corresponding *cis*- and *trans*-monoethenoic isomers, the monoethynoic acids,

and the differences in the heats of combustion for the several pairs of these acids, as compiled by Kharasch (3).

From the data in Tables 67 and 68 it is evident that both the experimental and calculated values for the heat of combustion of oleic acid are out of line with those for the related acids. Keffler (6) refers to the publications of Stohmann (1,7) wherein the heat of combustion of oleic acid was reported to be 2682.0 kcal. and that of solid elaidic acid as 2664.3 kcal. When these values are corrected according to the Landolt-Bornstein tables, and the value for elaidic acid calculated for the liquid state, as was done by Keffler, the two values become 2680.1 kcal. for oleic acid, and 2677.2 kcal. for elaidic acid, or a difference of 2.9 kcal. These values, although perhaps not entirely accurate, indicate that the *cis*-isomer possesses the higher heat of combustion in accordance with Stohmann's rule that the *cis*-isomer of a given pair of geometrical isomers should have the higher heat of combustion.

Keffler (6) determined the heats of combustion of oleic and elaidic acids, obtaining a mean value from four determinations of 9343 cal._{20°} per g., or 2638.9 kcal. per mole, for the solid isomer. The values for oleic acid varied from 9542 cal. per g., for a two-day-old sample, to 9142 cal. per g. for the same acid after two years, with various values in between depending on the age of the sample. The heat of combustion of a sample of freshly distilled oleic acid was found to be 9473 cal. per g. when determined within two hours of preparation. This value decreased hourly to 9446 cal. per g. during the first 24 hours after preparation, or a change of 26 cal. per g. These values have been calculated to a kcal. per mole basis and included in Table 69 together with other previously mentioned values for oleic acid.

TABLE 69
Heats of Combustion of Oleic and Elaidic Acids, Kcal. per mole

Oleic acid	Elaidic acid	Difference	Investigator
2663.6 ^a	2670.1 ^a	6.5	Kharasch
2681.8	2664.1	17.7	Kharasch
2657.0			
2680.1			
2695.1 ^b	2677.2	2.9	Stohmann-Keffler
2668.0 ^c	2638.9	56.2	Keffler
2659.5 ^d			Keffler

^a Calculated.

^b Fresh preparation.

^c Twenty hours after preparation.

^d Two years after preparation.

The different values for the heats of combustion of oleic and elaidic acids shown in Table 69 are not strictly comparable owing to differences in units employed in their calculations, but they are sufficiently so to indicate the fact that their heats of combustion were not accurately known up to 1930. The values obtained by different investigators reflect the difficulty of preparing and maintaining these acids in a pure state rather than a lack of precision in the experimental determination of the heats of combustion. It is significant that, with the exception of the lower value given by Kharasch (3), the heat of combustion found for oleic acid is higher than for elaidic acid; this is in accordance with other known facts concerning the relative stabilities of these two acids. It is obvious that the calculated values of the heats of combustion, if reversed, would be more nearly in accord with the experimental values.

Following the development of more rigorous methods of purifying oleic acid, Keffler (8,9) prepared a series of esters of oleic and elaidic acids and determined their heats of combustion with the results shown in Table 70.

TABLE 70
Heats of Combustion of Liquid Oleates and Elaidates
in Kcal._{15°} per Mole (8,9)

Alkyl radical	Oleate	Elaidate	Molecular heat of transformation
Methyl	2837.2	2835.7	+1.5
Ethyl	2988.2	2988.9	-0.7
Propyl	3146.2	3144.7	+1.5
Butyl	3302.3	3300.6	+1.7
Amyl		3456.5	

In each case the oleate was found to have the higher heat of combustion and the average isothermal heat of transition from oleate to elaidate was found to be about + 1.6 kcal. per mole.

(c) *Glycerides*

Few data are available for the heats of combustion of mono- and diglycerides which are especially significant with respect to the structural symmetry and stability of these compounds. Clarke and Stegeman (10) determined the heats of combustion of α - and β -monopalmitin which were found to be, respectively, 2778.78 and 2788.30 kcal. per mole for the reaction at one atmosphere pressure and 25°C., or -9.52 kcal. per mole for

the shift from the β -to the α -position. The calculated value for α -monomyristin is 2464.78 kcal per mole.

Stohmann and co-workers determined the heats of combustion of many fatty acids and glyceryl di- and triesters. These esters were prepared by Stohmann and Langbein (11) according to the method of Reimer and Will (12), and nothing is known concerning their structural configuration or homogeneity. The heats of combustion for glyceryl dierucate, m.p. 47°C., and dibrassidate, m.p. 67°C., were found to be 6979.0 and 6953.0 kcal._{15°}, respectively. The glyceride of the *cis*-isomer has the higher heat of combustion which is in accord with the known stability of such geometrical isomers. The glyceryl triesters reported are butyrate, 1941.1; laurate, 5706.3; myristate, 6650.3; brassidate, 10235.8(s); and erucate, 10264.7(s) kcal._{15°}. The classical work of Stohmann should be consulted for additional data and for more detailed information on the heats of combustion of the various compounds already mentioned, and for the natural fats, including lard, beef and mutton tallow, butter, and duck and goose fats.

3. Vapor Pressure and Related Properties

Of the various colligative properties of the higher fatty acids and esters none is so important theoretically and practically as vapor pressure and the related properties, boiling point and heat of vaporization. It is only since the 1930's that systematic determinations have been made of these important properties of the fatty acids, thereby placing our knowledge of the properties of these compounds on a par with that of other and much less important organic compounds.

(a) Saturated Acids

Lederer (13), one of the first to determine the molecular heats of vaporization and the heat of vaporization of fatty acids at atmospheric pressure, stated in an article published in 1930: "It appears almost incredible that, after fifty years of large-scale fatty acid distillation, data relative to these important properties are not known; at least they are not found in the literature." To this statement Lederer appended a footnote which reads: "Here might be mentioned a fact which is not without its humorous angle. A famous German equipment company, which required a knowledge of heats of vaporization of fatty acids for use in fabricating a condenser for a fatty acid still, turned to research chemists (specialists in fats and oils) for this information. One 'estimated' a heat of vaporiza-

tion of 100 calories, another regretted that he could not find a value in the literature. One explained that fatty acids had in general no heats of vaporization at all, since they could not be boiled without decomposition (at atmospheric pressure).'' In the interval since that time, a very considerable amount of reliable data has been accumulated, but our knowledge is not yet as complete as it might be.

Although now somewhat outmoded, and not too exact in many respects owing to the lack of reliable experimental data, portions of Lederer's work are given here as an example of the early (1930) treatment of the vapor pressure-temperature relationships of fatty acids.

Through the application of thermodynamic principles an equation can be derived for vapor pressure-temperature relation which can be brought to the form:

$$\ln p = -\lambda_0/RT + 1.75 \ln T - \epsilon T'/R + C \quad (1)$$

where p is the vapor pressure at any optional absolute temperature T ($^{\circ}\text{C.} + 273$), λ_0 the molecular heat of vaporization at absolute zero, R the gas constant, ϵ the temperature coefficient of the difference between specific heats in the liquid and gaseous state, and C the so-called "conventional chemical constant." If the natural logarithm, $\ln$, is replaced by the common logarithm, $\log$, and there is substituted for the gas constant its numerical value (1.985 cal./ $^{\circ}\text{C.}$), equation (1) becomes:

$$\log p = -\lambda_0/4.571 T + 1.75 \log T - \epsilon/4.571 T + C \quad (2)$$

From the data available in the literature (1930) for the boiling points of the higher fatty acids under different pressures, there can be calculated the values given in Table 71 which apply when the vapor pressure is measured in millimeters of mercury. The heat of vaporization at any absolute temperature T can be expressed approximately by the equation:

$$\lambda = (\lambda_0 + 1.75 RT - \epsilon T^2)(1 - p/P) \quad (3)$$

where P is the critical pressure, which lies between 30 and 40 atm. for the higher fatty acids. If accurate data are not available, equation (3) can still be used for calculation when the pressure is not too high. At atmospheric pressure the factor in the second term of equation (3) has a value varying but little from unity (about 0.97), and at 100 mm. pressure it is only 0.996.

A knowledge of the three constants, λ_0 , ϵ , and C , makes it possible to calculate over a very restricted temperature interval the vapor pressure at a given temperature, or what amounts to the same thing, the boiling

point of the fatty acid at a given pressure. These three constants, as reported by Lederer (13), are given for a series of fatty acids in Table 71.

TABLE 71
Calculated Constants Applicable to Vapor Pressure Equation
for Higher Aliphatic Acids (13)

Acid	λ_0	ϵ	C	λ_a	l_a	T_a	λ_a/T_a (calcd.)	Trouton
Capric	22990	0.0334	11.318	14660	85	543	27.0	22.3
Lauric	23590	0.0349	11.408	13740	68.5	574.6	23.9	22.5
Myristic	24960	0.0334	11.493	14700	67.5	601	24.5	22.8
Palmitic	26050	0.0326	11.568	15090	58.5	625	24.2	23.0
Stearic	27280	0.0317	11.636	15860	56	647	24.5	23.2
Oleic	26660	0.0304	11.340	16050	57	642	25.0	23.1
Erucic	29310	0.0264	11.458					

In addition, the molecular heat of evaporation at atmospheric pressure, λ_a , can be calculated by means of equation (3). The values for λ_a are given in column 5, Table 71, and in the next column are the heats of vaporization l_a of the fatty acids at atmospheric pressure in cal. per kg.

It should be noted that the heats of vaporization of fatty acids at pressures occurring in industrial practice are very often higher than those obtaining at atmospheric pressure. By means of equation (3) it is easy to calculate, for example, that lowering of the pressure from 1 atm. to 100 mm. increases the value of the heat of vaporization on the average 10 cal. per kg. (about 20%); lowering it to 5 mm. increases this value by an average of 20 cal. per kg. (about 40%). However, this is not important industrially because the increase in heat necessary for evaporation is small in comparison with the usual heat losses resulting from radiation, conduction, etc.

There are also given in Table 71 the absolute boiling points of the fatty acids at atmospheric pressure, T_a , as found in the literature (1930); also the proportion $\lambda_a:T_a$. This proportion should agree with the values given in the last column of Table 71 which were calculated on the basis of the Trouton-Nernst rule. From the fact that the value of this proportion is always greater than that calculated by the Trouton-Nernst rule, it may be concluded that the fatty acids in the liquid state are fairly completely associated, while in the vapor state the vapor density corresponds to their normal molecular weight.

With the aid of the data given in Table 71, the vapor pressures of the various acids at definite temperatures have been calculated and compared

in Table 72 with the values given in the Landholt-Bornstein tables. Since the constants are derived from the data at atmospheric pressure and at 100 mm. pressure, it is evident that the calculated and experimental values will agree at both these points. Their inclusion in Table 72 is, therefore, unnecessary. For oleic acid, pressures of 100 mm. and of 10 mm. were used for purposes of computation because of lack of accurate data at

TABLE 72
Vapor Pressure at Various Temperatures for
Several Fatty Acids According to Lederer (13)

Acid	Temperature, °K.	Vapor pressure, mm.	
		Calcd.	Found
Capric	458	45	50
	439	19.4	21
	426	10	10
Lauric	484	55	50
	472	32	35
	465	27	27
	462	23	24
	451	14.4	13.2
Myristic	506	54.6	50
	497	38.8	40
	493.7	34.8	35
	490.4	30.5	30
	486.2	25.9	25
	480.6	20.6	20
	467.7	11.9	12
Palmitic	463.8	10	10
	498	19.1	22.1
	493	15.8	15.7
	488	13.0	15
Stearic	505	8.7	15
Oleic	537	49	50
	523	29.5	30
	506	15.2	15

atmospheric pressure. In view of the good agreement between the calculated and the experimentally determined values, equation (3) was assumed to be reliable for use in calculating the boiling point, using the constants given by Lederer. It should be borne in mind, however, that at the time (1930) very few data were available in the literature by which this equation could be checked.

It is evident from Table 71 that the values of the constants for the various fatty acids do not differ greatly, and this is especially true of the temperature coefficient of specific heat, ϵ . It is evident that in equation (2) the terms, with the exception of the first and last, are merely correction factors, and it can be assumed therefore that the difference in the specific heats of the fatty acids in the liquid and vapor states is almost independent of temperature. Consequently, equation (2) may be written in a much simpler form, or a graphical method may be used in its place, thus obviating the necessity for calculations in many cases.

Inspection of equation (2) indicates that if both middle terms are disregarded, and the reciprocal values of the absolute temperatures are plotted as abscissas against the logarithms of the vapor pressures (in mm.) as ordinates, the result will be a straight line. If the middle terms are not disregarded, the plot of the data will depart slightly from a straight line, as is indicated in Figure 28. On the other hand, it can be assumed that, because of the small differences in the critical pressures of

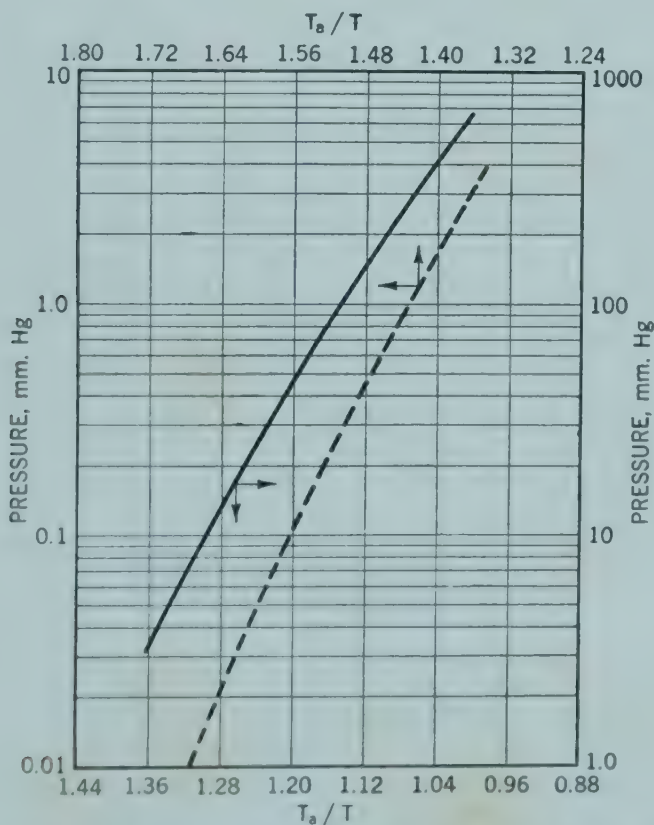


Fig. 28. Relation between vapor pressure and boiling points of the fatty acids (13).

the fatty acids, their boiling points comprise corresponding states (14,15). This is also the case at any temperature at which the quotient of the absolute boiling point and the temperature in question is the same; and the desired data for any fatty acid whatever can be read from such a graphical plot, at least with accuracy sufficient for engineering calculation, when only the boiling point at atmospheric pressure (or eventually at any other given pressure) is known.

The two curves reproduced in Figure 28 were obtained by plotting as abscissas the quotients of the absolute boiling points at atmospheric pressure divided by the observed temperatures at any other pressure (T_a/T), and plotting as ordinates the corresponding pressure in mm. The ordinates at the right (pressure in mm.) and the abscissas at the bottom (atmospheric boiling points divided by the required temperatures) are read from the solid line, the ordinates at the left and the abscissas at the upper edge are read from the broken line; the solid line is drawn over a pressure range of from 600 to 3 mm. of mercury, the broken line over a range from 4 to 0.01 mm. of mercury. The value and use of this graph are best illustrated by a few practical examples, as follows: At what temperature does stearic acid boil at a pressure of 20 mm., taking $T_a = 647^\circ\text{K}$. (374°C .) from Table 71? By reference to the solid line it is found that a pressure of 20 mm. corresponds to an abscissa of 1.25; T_a divided by 1.25 gives 517°K . or 244°C . As another example, it might be desired to know the pressure at which myristic acid would boil at a temperature of 288°C . (501°K .), $T_a = 601^\circ\text{K}$. (328°C .). T_a divided by 501°K . gives 1.20, for which abscissa the corresponding pressure is found to be 47 mm.

For problems occurring in industry, the solid line will be generally used in dry distillation, but for steam distillation involving the determination of the boiling point at a given pressure, or the vapor pressure at a given temperature, frequent use must be made of the broken line. In the case of steam distillation other data are necessary, namely, the proportion by weight of steam used for distillation to the amount of acid to be distilled. However, both pressure and temperature may be given and the problem may be to determine the proportion by weight of steam and fatty acid.

For steam distillation, Dalton's Law of Partial Pressure can be applied as a good approximation. If the total pressure is p , the partial pressure of the fatty acid is x , the molecular weight of the fatty acid is M (that of steam is 18), and the proportion by weight of steam to fatty acid is v , then, with an accuracy sufficient for industrial use, $v = 18(p - x)/Mx$. The method of calculation may be illustrated by the follow-

ing: At what temperature does palmitic acid boil at 100 mm. pressure when the proportion by weight of steam to acid is 1:1 ($v = 1$)? Here, $p = 100$, $M = 256$, and since $v = 1$, it can be calculated by means of the equation just given that $x = 6.6$ mm. At this ordinate (solid line) it is found that the abscissa is 1.318 and, therefore, the temperature sought ($T_a = 625$) if 625 divided by $1.318 = 475^\circ\text{K.} = 202^\circ\text{C.}$

It may be desired to know, for example, what pressure should be used to distill oleic acid ($M = 282$) at a temperature of 187°C. or 460°K. , with twice the amount of steam ($v = 2$). $T_a = 642$, and 642 divided by $460 = 1.39$. This abscissa corresponds to a partial pressure $x = 1.9$ mm. on the dotted line. By means of the above equation the desired total pressure p can be calculated as 61.4 mm. Another example might be to determine what proportion of water by weight should be used to distill stearic acid ($M = 284$) at a total pressure of 30 mm. and a temperature of 157°C. or 430°K. T_a divided by $430 = 1.50$. At this abscissa it is found from the broken line that the partial pressure is 0.3 mm.; therefore:

$$v = (18 \times 29.7)/(284 \times 0.3) = 6.2$$

therefore, more than six times as much water as fatty acid must be used.

Although sometimes desirable as a laboratory operation, distillation of a single pure fatty acid is very seldom conducted on an industrial scale, whereas distillation of mixtures of fatty acids is an important operation on both scales. In general, mixtures of fatty acids can be fractionated until a maximum boiling point is reached. At this temperature the mixture exhibits a constant boiling point and further separation by means of fractional distillation cannot be achieved.

Since Lederer published his article, additional data have become available with respect to the boiling points and vapor pressures of the fatty acids and their derivatives which may be applied as he has indicated in the solution of practical problems.

Gensecke (16) investigated the vapor pressure-temperature relations of the fatty acids from acetic to docosanoic over a limited pressure range (2 to 100 mm.) employing steam distillation under vacuum. The curves obtained by this means are reproduced in Figure 29, in which the temperatures in $^\circ\text{C.}$ are plotted as abscissas against the logarithms of the vapor pressures as ordinates. The vapor pressure curves obtained in this manner, although not as accurate as those obtained by the use of dry distillation, are nevertheless useful in cases where more accurate data are not available.

The most accurate determinations of the vapor pressure-temperature

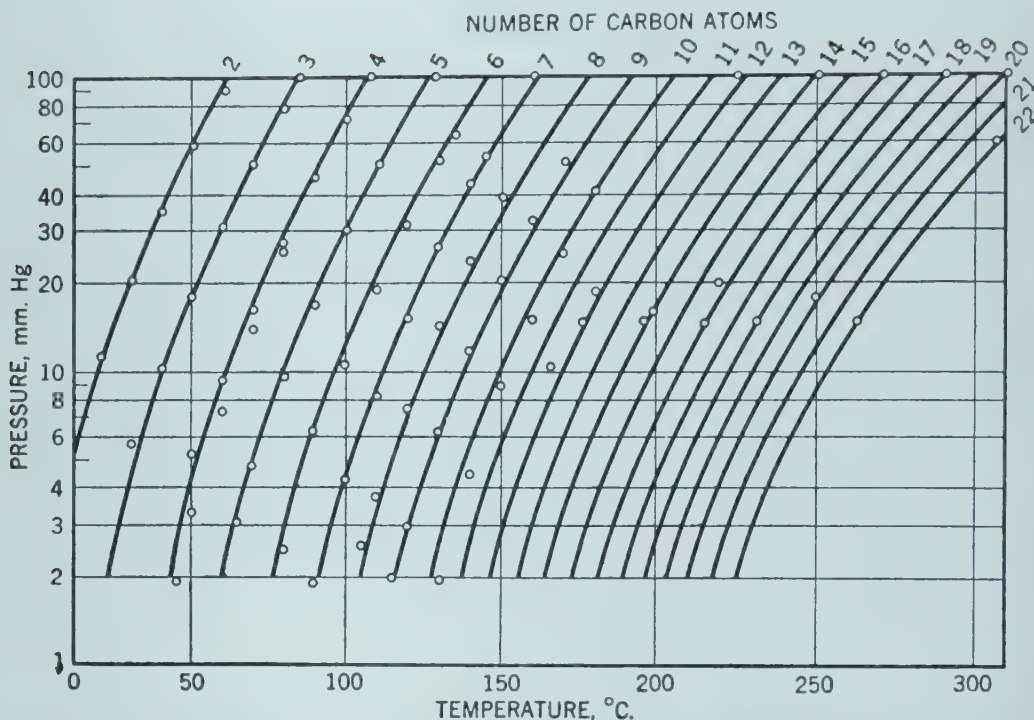


Fig. 29. Boiling points of the fatty acids under conditions of vacuum-steam distillation (16).

TABLE 73
Boiling Points in °C. of *n*-Fatty Acids (17)

No. of C atoms	Pressure, mm. (Hg)										
	1	2	4	8	16	32	64	128	256	512	760
6	61.7	71.9	82.8	94.6	107.3	120.8	136.0	152.5	171.5	192.5	205.8
7	74.9	85.3	96.3	108.3	121.1	135.2	150.8	168.2	187.5	209.3	223.0
8	87.5	97.9	109.1	121.3	134.6	149.2	165.3	183.3	203.0	225.6	239.7
9	98.9	109.6	121.2	134.0	147.5	162.4	178.8	196.9	217.4	240.9	255.6
10	110.3	121.1	132.7	145.5	159.4	174.6	191.3	209.8	230.6	254.9	270.6
11	119.8	131.1	143.3	156.5	170.8	186.1	203.1	222.2	243.8	268.7	284.0
12	130.2	141.8	154.1	167.4	181.8	197.4	214.6	234.3	256.6	282.5	298.9
13	139.9	151.5	164.2	177.8	192.2	207.9	225.8	245.9	268.6	295.4	312.4
14	149.2	161.1	173.9	187.6	202.4	218.3	236.3	257.3	281.5	309.0	326.2 ^a
15	157.8	169.7	182.8	196.8	212.0	228.1	246.4	268.0	292.7	321.2	339.1 ^a
16	167.4	179.0	192.2	206.1	221.5	238.4	257.1	278.7	303.6	332.6 ^a	351.5 ^a
17	175.1	187.6	200.8	214.9	230.7	247.9	266.6	288.4	314.3	343.8 ^a	363.8 ^a
18	183.6	195.9	209.2	224.1	240.0	257.1	276.8	299.7	324.8	355.2 ^a	376.1 ^a

^a Values obtained by extrapolation.

relationships for the fatty acids and their derivatives have been made by Ralston and co-workers, and by Jantzen and Erdmann. Pool and Ralston (17) determined the boiling points of the *n*-saturated fatty acids from C_6 to C_{18} over a range of pressures from 1 to 760 mm. Their results are reproduced in Table 73. These workers computed the data required to construct the corresponding vapor pressure-temperature curves which are reproduced in Figure 30. The graphic representation shows the effect of increasing chain length on the vapor pressure and the increasing difficulty of effectively separating fatty acid mixtures as the chain length increases.

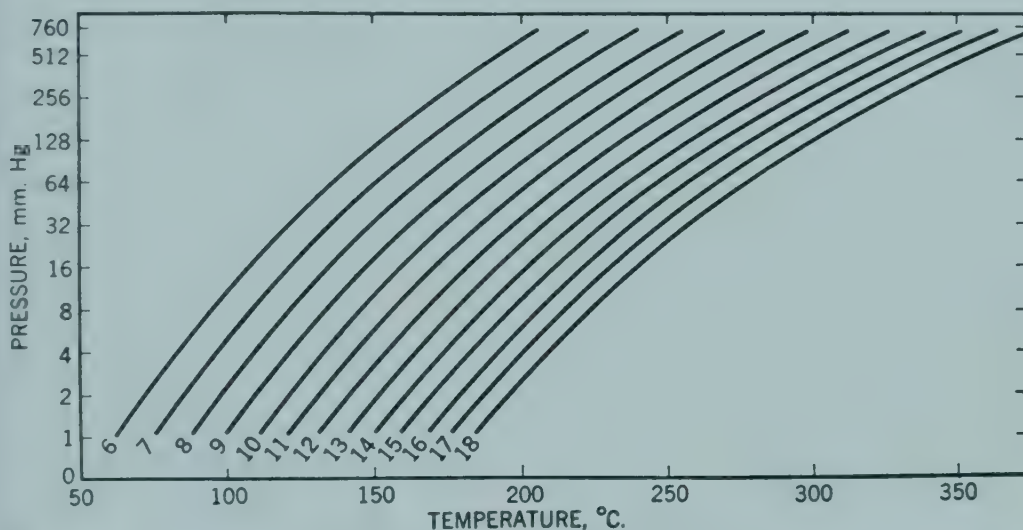


Fig. 30. Vapor pressure curves of the *n*-alkyl acids containing from 6 to 18 carbon atoms (17).

Jantzen and Erdmann (18) determined the boiling points of normal saturated fatty acids containing up to 30 carbon atoms, at pressures from 0.0001 to 760 mm. These workers also calculated the vapor pressure of the same series of fatty acids, by the equation

$$\Delta K_p = F (1/C_n)^{1/2}$$

where ΔK_p is the increase in boiling point per C atom added to the chain, C_n is the number of carbon atoms of the acid, and F is a pressure factor. The factor F at various ranges of pressure is given as follows: 0.0001

mm., F is 27.8; 0.001 mm., F is 29.2; 0.01 mm., F is 30.1; 0.1 mm., F is 34.8; 2 mm., F is 35.4; 4 mm., F is 36.1; and 8 mm., F is 37.0.

The boiling points are given in the form of a plot of temperature vs. pressure, which plot is reproduced in Figure 31.

The authors state that the curves of this figure may be used to estimate the boiling points of acids other than the normal saturated ones provided one point of their vapor pressure diagram is known, because it may be assumed that the two curves will be parallel over a certain range of pressure.

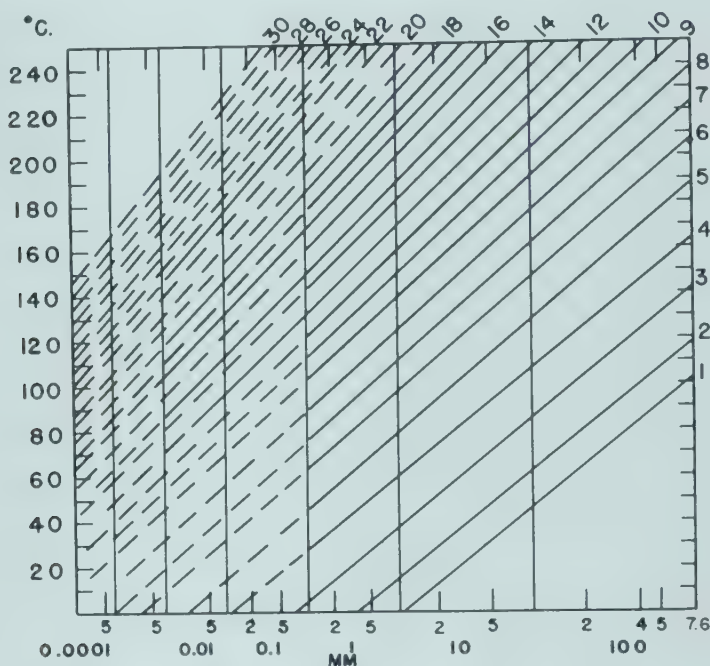


Fig. 31. Boiling points of fatty acids vs. pressure. Carbon atoms indicated at upper end of each line. Unbroken lines are experimental values, broken lines are calculated values.

Table 74 gives the boiling points of the common saturated fatty acids through stearic at several selected pressures, as taken from the plotted values of Jantzen and Erdmann.

The boiling points at atmospheric pressure of several short chain acids, and of some isomeric branched-chain acids are reported by Alpert and Elving (19) and by Hancock, *et al.* (5), and are listed in Table 75.

Cramer (20) determined the vapor pressures of the even-numbered

TABLE 74
Boiling Points (°C.) of Normal Aliphatic Acids at Various Pressures (18)

Carbon atoms	Pressure, mm. (Hg)						
	0.01	0.1	1.0	2.0	5.0	10.0	100.0
1							44.0
2					6.0	17.5	62.5
3			4.5	14.5	28.0	39.5	84.5
4			26.0	35.5	50.0	61.5	107.5
5		16.5	44.0	54.0	68.0	80.0	127.0
6	11.5	34.0	62.0	72.5	86.5	98.5	146.5
7	22.0	45.5	74.5	85.5	100.0	112.5	162.5
8	33.5	57.5	87.5	98.5	113.5	126.5	177.0
9	45.0	69.0	99.5	110.5	126.0	138.5	190.0
10	55.0	79.0	110.0	121.5	137.0	150.5	202.5
11	63.5	89.0	120.5	132.0	148.5	161.5	214.5
12	73.0	98.5	131.0	142.0	158.0	172.5	226.5
13	81.5	107.0	140.5	151.5	168.0	182.5	238.0
14	89.0	116.0	149.5	161.0	177.5	192.5	249.0
15	97.0	124.0	158.0	170.0	186.5	202.5	
16	105.0	132.5	167.0	179.0	197.0	211.5	
17	112.5	140.5	175.5	187.5	206.0	220.0	
18	119.5	147.5	183.5	196.0	213.0		

TABLE 75
Boiling Points of Short-Chain and Branched-Chain Acids

Acid	B.p. ₇₆₀ , °C.
Formic	100.8 ^a
Acetic	118.1 ^a
Valeric	186.7 ^b
α-Methyl butyric	176.5 ^b
Isovaleric	176.7 ^b
Pivalic	164.4 ^b

^a Alpert and Elving (19).

^b Hancock *et al.* (5).

fatty acids from caproic to stearic by the static method of Smith and Menzies (21). By means of the equation:

$$d \ln p / d(1/T) = - W/R$$

where W is the heat vaporization per gram mole, T the absolute temperature, and R the gas constant, he calculated the heats of vaporization of the acids at the temperatures shown in Table 76.

TABLE 76
Calculated Heats of Vaporization of Saturated Acids
at Various Temperatures (20)

Acid	Temperature, °C.	Heats of vaporiza- tion, cal./g.	Acid	Temperature, °C.	Heats of vaporiza- tion, cal./g.
Caproic	94	133	Lauric	164	97
	135	129		247	77
	190	113	Myristic	182	93
Caprylic	134	116		209	87
	172	108		243	75
	224	97	Palmitic	202	84
Capric	145	99		244	76
	187	99	Stearic	242	67
	246	85			

If desired, the heats of vaporization can be calculated from the data of Pool and Ralston (17) by the use, in small pressure and temperature intervals, of the integrated form of the approximate Clausius-Clapeyron equation:

$$L = [\log p_2/p_1 (4.576) T_2 T_1]/T_2 - T_1$$

where L is the heat of vaporization; p_1 and p_2 , and T_1 and T_2 are pressures and temperatures, respectively. Calculated values in the range of 2 to 8 mm. pressure are, for example, 80, 86, 91, and 98 cal. per g. for stearic, palmitic, myristic, and lauric acids, respectively.

TABLE 77
Boiling Points (° C.) at Atmospheric Pressure of Alkyl Esters of
Low Molecular Weight Saturated Aliphatic Acids (22)

Alkyl radical	For- mates	Ace- tates	Pro- pion- ates	Butyr- ates	Valer- ates	Hexo- ates	Hepto- ates	Octo- ates
Methyl	31.8	57.1	79.9	102.3	127.3	149.5	172.5	192.9
Ethyl	54.3	77.1	99.1	121.3	145.5	166.6	187.5	205.8
Propyl	81.3	101.6	123.4	143.0	167.5	185.5	206.4	224.7
Butyl	106.8	126.5	145.4	164.4	185.6	204.3	225.1	240.5
Amyl	130.4	147.6		184.8	203.7	222.2		
Hexyl	153.6	169.3		205.1	223.8			
Heptyl	176.7	191.5	208.1	225.2	243.6	259.4	274.0	289.8
Octyl	198.1	210.1	226.4	244.5	260.2	268.2	290.4	305.9

The foregoing data relative to the experimental and calculated values for the boiling points and heats of vaporization represent a very great improvement in our knowledge of these properties of the fatty acids in comparison to that available in 1930.

(b) *Alkyl Esters of the Fatty Acids*

The boiling points at atmospheric pressure of the alkyl esters of the lower molecular weight fatty acids are well known as indicated by the compilation of Reid (22) which is reproduced in Table 77. Althouse and Triebold (23) determined the boiling points of the methyl esters of the even-numbered, saturated acids from caproic to stearic, over the pressure range of 2 to 40 mm. as shown in Table 78. Vapor pressures for each

TABLE 78
Boiling Points (° C.) of Methyl Esters of Saturated Aliphatic
Acids at Several Pressures (23)

Methyl ester	Pressure, mm. (Hg)						
	2	4	6	8	10	20	40
Caproate	15	26	33	38	42	55	70
Caprylate	45	58	65	71	76	89	106
Caprate	77	89	97	103	108	123	139
Laurate	100	113	121	128	134	149	166
Myristate	127	141	150	157	162	177	197
Palmitate	148	162	172	177	184	202	•
Stearate	166	181	191	199	204	•	•

• Decomposes.

TABLE 79
Decomposition Pressures and Temperatures
of Methyl Esters of Fatty Acids (23)

Methyl ester	Pressure, mm. (Hg)	Temperature, ° C.
Caproate	>760	>150
Caprylate	>760	>193
Caprate	>760	>224
Laurate	160	204
Myristate	60	205
Palmitate	25	151
Stearate	18	221
Oleate	16	217
Linoleate	11	208

ester were determined by the dynamic method of Ramsay and Young (24); the corresponding vapor pressure curves were constructed by plotting the reciprocal of the absolute temperature $\times 1000$ against the logarithm of the pressure in millimeters of mercury. The curves, thus constructed, were extrapolated to 760 mm. pressure as shown in Figure 32. These authors also determined the decomposition pressures and temperatures of the same series of esters as shown in Table 79.

The boiling points of the methyl, propyl, and isopropyl esters of the

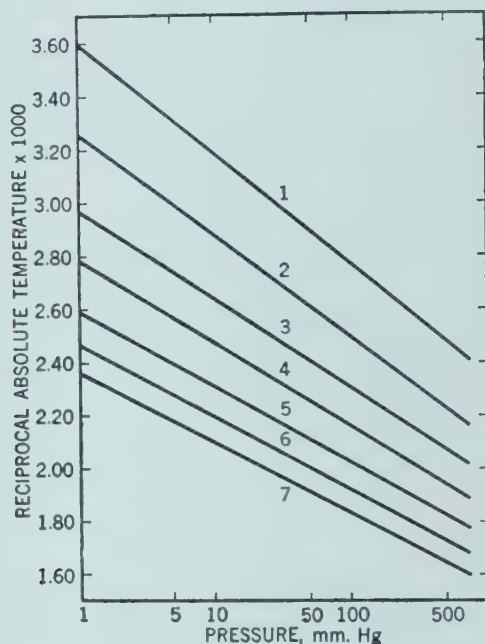


Fig. 32. Vapor pressure curves of methyl esters of the even-numbered fatty acids from caproic to stearic (23): (1) methyl caproate; (2) methyl caprylate; (3) methyl caprate; (4) methyl laurate; (5) methyl myristate; (6) methyl palmitate; (7) methyl stearate.

same series of acids were determined at pressures from 2 to 100 mm. by Bonhorst *et al.* (25) as indicated in Table 80.

Subsequently, Norris and Terry (26) published the results of their determinations of the boiling points of the methyl esters of myristic, palmitic, stearic, oleic, and linoleic acids over the pressure range of 1 to 20 (Table 81). The corresponding heats of evaporation were calculated by application of the Clausius-Clapeyron equation and the results were compared with those of the corresponding acids. Reference to these data in

TABLE 80

Boiling Points ($^{\circ}$ C.) of Methyl, Propyl, and Isopropyl Esters of Fatty Acids (25)

Ester	Pressure, mm. (Hg)						
	2	4	6	8	10	50	100
<i>Methyl</i>							
Caproate	16.8	27.5	34.1	38.8	42.8	74.2	90.7
Caprylate	51.5	62.5	68.9	73.8	77.8	110.0	125.6
Caprate	78.7	90.8	98.1	103.3	108.0	142.8	160.6
Laurate	102.8	116.0	124.4	130.4	135.0	173.9	192
Myristate	127.1	141.3	150.3	156.6	161.8	202.8	
Palmitate	148.5	163.2	172.6	179.2	184.8		
Stearate	169.4	184.6	193.6	198.8	206.6		
<i>Propyl</i>							
Caproate	42.9	54.2	60.9	65.9	70.2	103.8	120.3
Caprylate	70.5	82.3	90.0	94.1	100.0	135.0	152.6
Caprate	96.8	109.7	117.8	123.7	128.5	166.6	185.6
Laurate	123.7	138.1	147.0	153.3	156.8	200.2	
Myristate	147.0	161.7	171.0	177.6	182.8		
Palmitate	166.0	181.6	191.4	198.2	203.6		
Stearate	186.8	200.8	a				
<i>Isopropyl</i>							
Caproate	34.1	44.9	51.5	52.5	60.4	93.4	109.4
Caprylate	65.0	76.7	84.1	89.3	93.8	128.6	146.1
Caprate	90.0	102.5	110.5	116.5	121.1	159.4	177.6
Laurate	117.4	131.3	139.8	145.8	151.0	191.4	
Myristate	140.2	154.4	163.6	170.4	175.6		
Palmitate	160.0	175.4	184.8	191.6	197.1		
Stearate	181.6	197.5	207.0	a			

a Decomposition zone.

TABLE 81

Boiling Points ($^{\circ}$ C.) of Methyl Esters at Several Pressures (26)

Methyl ester	Pressure, mm. (Hg)				
	1	2	5	10	20
Myristate	114	125	143.5	157.5	172.5
Palmitate	136	149	166.5	180.5	196.5
Stearate	155.5	170	189.5	204.5	222
Oleate	152.5	166.5	186	201	218.5
Linoleate	149.5	163	182.5	198	215

Table 82 indicates that the latent heats of vaporization of myristic, palmitic, and stearic acids are 3200 to 3800 cal. per mole greater than those of the corresponding methyl esters.

TABLE 82
Heats of Vaporization for Methyl Esters and Fatty Acids (26)

Esters	L_v , cal./mole	Acids	L_v , cal./mole
Myristate	17,550	Myristic	20,800 ^a
Palmitate	18,900	Palmitic	22,100 ^a
Stearate	19,000	Stearic	22,800 ^a
Oleate	18,900		
Linoleate	18,750		

^a Calculated from data of Pool and Ralston.

Scott and co-workers (27) carefully determined the boiling points of the methyl esters of the saturated acids caprylic through stearic, and of the unsaturated acids oleic, linoleic, and linolenic, employing a tensimeter. The materials were carefully prepared and purified, and the boiling points determined at various pressures. From these data the boiling points at comparable pressures were calculated with the results given in Table 83. The calculated values were within $\pm 0.2^\circ\text{C}$. of the experimentally determined boiling points. The calculated heats of vaporization of these esters at 1 mm. pressure, are also included in Table 83.

TABLE 83
Calculated Boiling Points ($^\circ\text{C}$.) and Heats of Vaporization at
1 mm. of the Methyl Esters of Some Fatty Acids (27)

Methyl ester	Pressure, mm. (Hg)								Heat of vaporization, kcal./mole
	0.1	0.2	0.4	0.6	1.0	2.0	4.0	6.0	
Caprylate	...	...	...	30.7	37.9	48.2	59.5	66.4	13.37
Caprate	35.5	43.8	52.9	58.5	66.0	77.0	89.1	96.6	15.07
Laurate	59.6	68.5	78.1	84.0	92.0	103.5	116.1	124.1	16.57
Myristate	81.7	90.5	100.2	106.3	114.5	126.7	140.2	148.8	17.94
Palmitate	101.8	111.6	122.1	128.7	137.3	150.0	163.7	172.3	19.16
Stearate	121.5	131.6	142.5	149.2	158.2	171.2	185.4	194.3	20.47
Oleate	118.2	128.0	138.8	145.5	154.4	167.4	181.7	190.8	20.17
Linoleate	117.0	127.2	138.2	145.0	154.0	167.1	181.3	190.2	19.97
Linolenate	118.4	128.5	139.3	146.1	155.0	168.0	182.2	191.1	20.20

Stage (28) applied to the data for the boiling points of the methyl esters of fatty acids obtained by Bonhorst *et al.* (25) and Scott *et al.* (27), a method of correction and estimation, considering each ester in relationship to the whole homologous system. These corrected values are given in Table 84.

The ease with which the methyl esters of the consecutive even-numbered saturated acids can be separated by distillation is apparent from the fact that at a given pressure, the boiling points differ by 20° to 30°C.

TABLE 84
Boiling Points (°C.) of the Methyl Esters of Saturated
n-Fatty Acids at Various Pressures (28)

No. of C atoms	Pressure, mm. (Hg)							
	0.1	0.4	1.0	2.0	4.0	6.0	10.0	100.0
1	-92.3							
2	-77.9							9.1
3	-62.8							28.6
4	-49.0						6.9	50.0
5	-34.8			0.9	11.0	16.9	24.3	70.2
6	-20.1		6.4	17.0	27.8	34.1	42.1	91.0
7	-5.6	10.1	22.3	32.2	43.4	50.7	59.8	109.9
8	8.0	25.2	37.5	48.0	59.5	66.6	76.0	128.0
9	21.8	38.8	52.1	62.3	74.4	81.9	91.8	144.8
10	35.0	53.2	66.0	77.0	89.3	96.2	106.6	161.4
11	47.9	65.4	79.5	89.9	102.3	110.2	120.8	178.0
12	60.0	78.3	92.3	103.7	115.9	121.6	134.0	191.7
13	71.0	90.3	103.9	116.2	128.7	137.1	148.3	207.0
14	83.0	101.2	114.8	127.0	140.0	148.8	160.8	222.0
15	92.3	111.9	127.1	138.9	151.4	160.0	171.8	
16	102.1	122.1	137.0	148.9	162.9	172.0	183.8	
17	112.1	133.0	148.1	150.2	174.2	183.0	194.6	
18	122.0	142.6	158.0	171.4	185.3	194.3	206.0	

In the case of the methyl esters of the three commonly occurring C₁₈ mono-, di- and trienoic acids, the largest difference in the boiling points of any pair of these esters at a given pressure is 1.4°C.

The vapor pressures of a series of ethyl esters and alkyl acetates were determined by Shigley *et al.*, (29), using a semimicro method. The boiling points of these esters at several pressures are given in Table 85.

TABLE 85
Boiling Points (° C.) of Ethyl Esters of Saturated Aliphatic Acids and
of Several Alkyl Acetates at Various Pressures (mm. Hg) (29)

Ester	2	5	10	20	40	100
Ethyl caproate	27.1	42.2	54.5	67.7	82.2	103.0
Ethyl caprylate	57.4	73.7	87.0	101.8	117.6	140.8
Ethyl caprate	86.8	103.8	117.9	133.1	149.7	174.0
Ethyl laurate	113.8	131.3	146.0	161.5	178.4	
Ethyl myristate	134.8	153.3	168.7	184.8		
Ethyl palmitate	156.5	176.2	192.6			
Ethyl stearate	181.1	195.6				
Hexyl ethanoate	31.0	45.6	58.1	71.4	86.1	107.4
Octyl ethanoate	61.5	77.6	91.0	105.5	121.2	144.0
Decyl ethanoate	90.5	107.4	121.3	136.0	152.1	175.9
Dodecyl ethanoate	125.9	133.9	148.3	164.0	180.6	
Tetradecyl ethanoate	138.5	157.5	172.7	189.0		
Hexadecyl ethanoate	158.0	178.4	196.0			
Octadecyl ethanoate	177.2					

In Table 86 there are collected the melting points, boiling points at various pressures, and densities of several synthetic and some normal aliphatic alcohols (30).

TABLE 86
Boiling Points (°C.) and Densities of Several Saturated
Monohydric *n*-Aliphatic Alcohols (30)

Alcohol	Melting point, °C.	Pressure, mm. (Hg)			Density
		750	15	0.25	
Capryl	6.0	232	120 ₁₂		0.8297/20
Lauryl	23.9	257	150 ₂₀		0.8309/24
Myristyl	37.6	286	171.5		0.8236/38
Cetyl	49.1		190		0.8197/50
Stearyl	57.9		210	153.5	0.8124/59

The increasing use of plastics has created a use for vinyl esters of fatty acids. A series of vinyl esters was prepared and properties determined by Sasin and co-workers (30a), as given in Table 86a. (See also Swern *et al.* (30b).)

TABLE 86a
Some Properties of Vinyl α -Bromo Esters (30a)

R	Boiling point,		Refractive index, n_D^{30}	Density, d_4^{30}	Molecular refraction
	$^{\circ}\text{C.}$	Mm. (Hg)			
H—	50–51	9.0 ^a	1.4692	1.5414	29.88
CH ₃ (CH ₂) ₃ —	84–86	2.8 ^a	1.4588	1.2360	48.46
CH ₃ (CH ₂) ₆ —	66–67	0.15 ^a	1.4608	1.1566	62.39
CH ₃ (CH ₂) ₇ —	92–94	0.20 ^b	1.4612	1.1298	67.03
CH ₃ (CH ₂) ₉ —	116–117	0.20 ^b	1.4617	1.0933	76.32
CH ₃ (CH ₂) ₁₁ —	137–139	0.25 ^b	1.4627	1.0699	85.61
CH ₃ (CH ₂) ₁₃ —	165–167	0.15 ^b	1.4633	1.0554	94.89
CH ₃ (CH ₂) ₁₅ —	190–192	0.10 ^b	1.4641	1.0304	104.2

^a Distilled through a heated, jacketed Vigreux column, 60 cm. long.

^b Distilled through a short Claisen head filled with glass tubing.

(c) *Unsaturated Acids and Esters*

Except for oleic acid and the methyl esters of oleic, linoleic, and linolenic acids, few data are available relative to the vapor pressure-temperature relationships of the unsaturated fatty acids and esters.

TABLE 87
Boiling Points of Oleic Acid and Methyl Oleate

Oleic acid				Methyl oleate		
Pressure, mm.		B.p., °C.	Ref.	Pressure, mm.	B.p., °C.	Ref.
Obs.	Calcd.					
1.2		200	31	1	152.5	26
5.0		215	31	1	154.4	27
10.0		225	31	2	166.5	26
15.0		234	31	2	166.2	23
15.2	15	233	13	2	167.4	27
29.5	30	250	13	4	182	23
49	50	264	13	4	181.7	27
				5	186	26
				6	192	23
				6	190.8	27
				8	201	26
				8	199.5	23
				10	205.3	23
				20	218.5	26

Boiling points for oleic acid have been reported, among others, by Lederer (13) and Brown and Shinowara, (31), and for methyl oleate by Althouse and Triebold, (23), Norris and Terry (26), and Scott *et al.* (27) as indicated in the compilation in Table 87.

Owing to the thermal instability of the higher polyethenoic acids, accurate boiling point determinations can only be made over a limited temperature-pressure range. Boiling points have been reported for methyl linoleate by Norris and Terry (26), Althouse and Triebold (23), Scott *et al.* (27), and McCutcheon (32); and for methyl linolenate by McCutcheon (33) and Scott *et al.* (27). These data have been collected in Tables 88 and 89.

TABLE 88
Boiling Points (°C.) of Methyl Linoleate and Methyl Linolenate

Pressure, mm.	Linoleate	Ref.	Linolenate	Ref.
1	149.5	26	155.0	27
1	154.0	27		
2	166.5	23	168.0	27
2	163	32		
2	167.1	27		
2.5	175	32	174	33
4	182.4	23	184	33
4	181.3	27	182.2	27
4.5	187.5	26		
5	182.5	26		
6	193.0	23	191.1	27
6	193.5	32		
6	190.2	27		
8	199.9	23		
10	206.0	23		
10	198	26		
11			211	33
12	212	32		
15			218	33
17	224	32		
20	215	26		

While in general the boiling points of methyl linoleate shown in Table 88 are fairly consistent, some inconsistencies are noted, especially at the higher temperatures and pressures where partial decomposition may have occurred.

TABLE 89
Boiling Points ($^{\circ}\text{C}.$) of the Methyl Esters of Unsaturated
Fatty Acids (27)

Pressure, mm.	Oleate	Linoleate	Linolenate
0.1	118.2	117.0	118.4
0.2	128.0	127.2	128.5
0.4	138.8	138.2	139.3
0.6	145.5	145.0	146.1
1	154.4	154.0	155.0
2	167.4	167.1	168.0
4	181.7	181.3	182.2
6	190.8	190.2	191.1

Althouse and Triebold (23) and Norris and Terry (26) determined the vapor pressures of methyl oleate and methyl linoleate and constructed the vapor pressure curves shown in Figures 33 and 34.

It is apparent from inspection of the vapor pressure curves of the saturated esters that the lower members should be readily separable by dis-

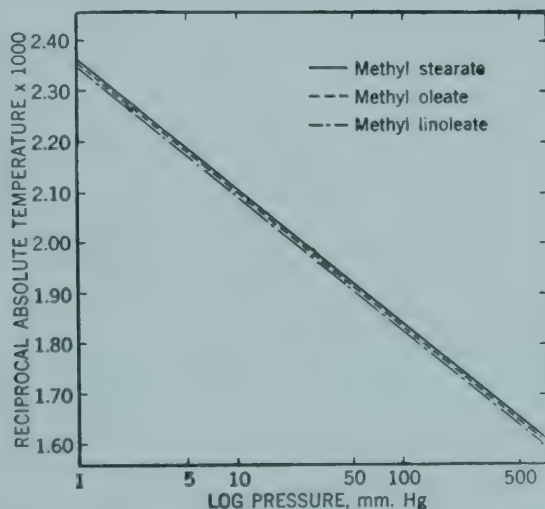


Fig. 33. Vapor pressure curves of methyl stearate, methyl oleate, and methyl linoleate according to Althouse and Triebold (23).

tillation and that, as the series is ascended, this type of separation should become increasingly difficult. Comparison of the vapor pressure curves of methyl stearate, methyl oleate, and methyl linoleate indicates that their separation by distillation should be very difficult.

Furthermore, comparison of the data of Althouse and Triebold with those of Norris and Terry reveals several inconsistencies, principally in the relative positions of the vapor pressure curves for the methyl esters of the three C_{18} -acids. Althouse and Triebold found them to be in descending order stearate-oleate-linoleate, whereas Norris and Terry found them to be linoleate-oleate-stearate. According to the latter authors, these discrepancies are due to inaccuracies in the data of Althouse and Triebold. In substantiation of this view, they state that the order of Althouse and Triebold's vapor pressure curves is contrary to practical experience since they obtained 95% methyl oleate in the first fractions from the distillation of a methyl oleate-methyl stearate mixture and

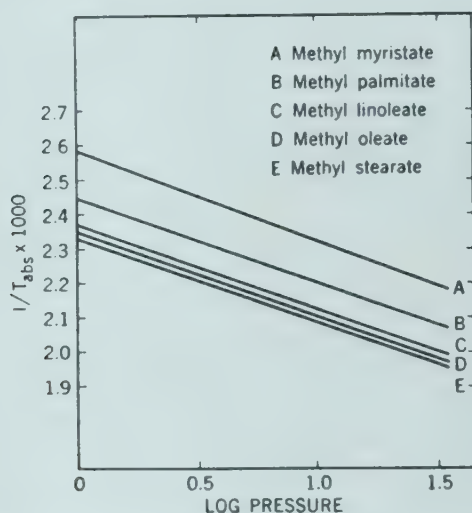


Fig. 34. Vapor pressure curves of saturated and unsaturated methyl esters according to Norris and Terry (26).

some concentration of methyl linoleate in the first fractions from the distillation of a methyl linoleate-methyl oleate mixture. The data of Norris and Terry agree with those of Scott and co-workers (27).

The discrepancies between the results of these three groups of workers attest to the difficulties encountered in the separation by distillation of the higher fatty acids and esters of the same chain length. It seems safe to say that, while the vapor pressure of a fatty acid or ester is primarily dependent upon its chain length, in the range of 1–20 mm. pressure methyl linoleate boils about 3° lower than methyl oleate, which in turn boils about 3° lower than methyl stearate.

Only a few scattered values for the boiling points have been reported for other than the three previously mentioned unsaturated acids. Typical

of these data are the values collected in Table 90 which represent, for the most part, observations made during fractional distillation of mixtures

TABLE 90

Boiling Points of Some Unsaturated Fatty Acids and Methyl Esters^a

Acid	Acid b.p., °C.	Methyl ester b.p., °C.	Acid	Acid b.p., °C.	Methyl ester b.p., °C.
9-Decenoic	142 ⁴	115-16 ¹²	Erucic	281 ³⁰	225 ⁵ , 169-70 ¹
Dodecenoic		89-90 ¹	Ricinoleic		225 ¹⁰
5-Tetradecenoic		110-11 ¹	Hydnocarpic		203 ²⁰
Myristoleic		108-09 ¹	Chaulmoogric	248 ²⁰	227 ²⁰
Palmitoleic		134-35 ¹	Gorlic		219 ¹²
Elaidic		150 ¹	Eleostearic	235 ¹²	
Petroselinic		150 ¹	Arachidonic		160-65 ¹
Eicosenoic		160 ¹	Clupanodonic		170-75 ¹

^a Superscripts refer to pressures in millimeters of mercury.

TABLE 91

Boiling Points of α -*n*-Alkyl-Branched Stearic Acids and
Methyl Esters of Alkyl-Branched Palmitic and Stearic Acids (34)

α - <i>n</i> Alkyl stearic acid			Methyl esters of alkyl-branched acids				
			Position of branch- ing	Palmitic		Stearic	
Branching alkyl group	Boiling point, °C.	Pres- sure, mm.		Boiling point, °C.	Pres- sure, mm.	Boiling point °C.	Pres- sure, mm.
Methyl	176	0.5	2	160	0.5		
Ethyl	182	0.5	3	174-176	0.5	175	0.1
Propyl	189	0.5	4	159-162	0.2	175	0.1
Butyl	197	0.5	5	158-160	0.2	174	0.1
Amyl	205	0.5	6	173	2.0	172	0.1
Hexyl	210	0.5	7	180-181	2.0	173	0.1
Heptyl	216	0.5	8	168-170	0.5	174	0.1
Octyl	221	0.4	9	188	0.4	171	0.1
Nonyl	225	0.4	10	189	1.5	188	0.5
Decyl	230	0.4	11	187-188	0.4	174	0.1
Hendecyl	209	0.1	12	189	2.0	194	0.6
Dodecyl	214	0.1	13	186	0.4	190	0.5
			14	173	0.5	182	0.4
			15	176	0.5	183	0.4
			16			182	0.4
			17			180	0.3

of fatty acids or esters containing the specific compound as the principal product.

(d) *Branched-Chain and Dibasic Acids and Esters*

The homologous series of α -*n*-alkyl-branched stearic acids from α -methyl to α -dodecyl and the branched-chain methyl esters of palmitic and stearic acids were prepared by Weitzel and Wojahn (34). The boiling points of these materials at various pressures are given in Table 91. Weitkamp (35) determined the boiling points at 1.95 mm. of the methyl esters of normal and methyl-branched acids, and found that the esters of branched acids (iso) had boiling points 3 to 4°C. lower than normal esters of the normal acids. These results are given in Table 92. Hancock

TABLE 92
Boiling Points of the Methyl Esters of Normal and Methyl-Branched
Aliphatic Acids at 1.95 mm. (35)

Methyl ester of <i>n</i> -acid	B.p., °C.	Methyl ester of iso-acid	B.p., °C.	Methyl ester of iso-acid	B.p., °C.
Caprate	79	Isocaprate	75	6-Methyloctanoate	60
Laurate	104.5	Isolaurate	100.5	8-Methyldecanoate	88
Myristate	128.5	Isomyristate	124.5	10-Methyldodecanoate	112.5
Palmitate	150	Isopalmitate	146.5	12-Methyltetradecanoate	136
Stearate	170	Isostearate	166.5	14-Methylhexadecanoate	156.5
Arachidate	188	Isoarachidate	185	16-Methyloctadecanoate	176
Behenate	205.5	Isobehenate	202.5	18-Methyleicosanoate	194
Lignocerate	222	Isolignocerate	219	20-Methyldecosanoate	211
Cerotate	237	Isocerotate	234	22-Methyltetracosanoate	227
				24-Methylhexacosanoate	241.5
				28-Methyltriacontanoate	266

and co-workers (5) determined the boiling points of the methyl and ethyl esters of the normal and isopentenoic acids listed in Table 93.

TABLE 93
Boiling Points (°C.) at Atmospheric Pressure of the
Methyl and Ethyl Esters of the Pentanoic Acids (5)

Acid	Methyl ester	Ethyl ester
Valeric	127.9	144.4
α -Methyl butyric	115.4	132.9
Isovaleric	117.4	135.4
Pivalic	101.9	118.4

Vogel (36) prepared the alkyl esters of a series of aliphatic monocarboxylic acids and the dialkyl esters of three dibasic acids for the determination of physical properties. The products were distilled, the middle fractions collected and their boiling points determined with the results given in Table 94.

TABLE 94
Boiling Points of Alkyl Esters of Mono- and Dicarboxylic Acids (36)

Esters	Methyl		Ethyl		<i>n</i> -Propyl		Butyl		Amyl	
	°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.
Formate			53.5	767	81.5	768	106.5	765	130.5	753
Acetate	56	754	77	770	101.5	767	125	755	148	762
Propionate	79	762	98.5	763	122	767				
<i>n</i> -Butyrate	103	774	121	774	142.5	772	165.5	773	185	757
Isobutyrate	91.5	761	110	762	134	752	156	762		
<i>n</i> -Valerate	126.5	756	144	762	163.5	750	184	753	202	749
Isovalerate	115.5	760	134	771	156	755	175.5	755		
Caproate	148.5	760	164.5	752						
Heptoate	171	761	185.5	764						
Caprylate	192	759	205.5	742						
Caprate	228	758	241.5	760	115	4.5	123	4		
Laurate	261.5	766	272.5	764	140	4	153.5	4.5		
Oxalate ^a			183.5	764	211	749	242	773	139	9
Succinate ^a	195	759	81	3	121	3	129	2		
Adipate ^a	120.5	17	134.5	17	146	9	158.5	7	185.5	10

^a Diesters.

The boiling points at reduced pressure of the ethyl esters of various other branched-chain acids have been reported. For example, Prout and Cason (37) reported boiling points for ethyl 10-keto-14 ethylhexadecanoate and ethyl 9-keto-15 ethylheptadecanoate as 192–196°C. at 1 mm., and 175–181°C. at 0.5 mm., respectively. Cason and Sumrell (38) reported the boiling point of ethyl 4-methyloctadecanoate to be 194.5–195.5°C. at 3.75 mm. pressure. This was found during the course of distillation of a mixture of the former and ethyl nonadecanoate. The boiling point of the latter at 3.75 mm. mercury is 198–198.5°C. Other boiling points reported by Cason *et al.* (39) are ethyl 3-methyloctadecanoate, 186–188°C. at 4 mm.; ethyl 3-methyltetracosanoate, 219–222°C. at 1.4 mm.; and ethyl 4-methyloctadecanoate, 163–164°C. at 1 mm.

Granoyskaya (40) reported the vapor pressures at three temperatures for several dibasic acids as indicated in Table 95.

TABLE 95
Vapor Pressures of Some Dibasic Acids (40)

Acid	Vapor pressure, mm.		
	18.5°C.	32.7°C.	47.0°C.
Oxalic	0.00081	0.00306	0.00780
Malonic	0.00109	0.00404	0.01571
Succinic	0.00223	0.00896	0.03317
Glutaric	0.01655	0.04434	0.11406
Adipic	0.07278	0.14464	0.28506

(e) *Glyceryl Esters*

Perry *et al.* (41) determined the boiling points for a number of molecularly distilled and recrystallized triglycerides from tributyrin to tristearin. In most cases a straight-line relationship was observed between temperature and pressure. The boiling points corresponding to pressures of 1 μ and 50 μ are given in Table 96.

TABLE 96
Boiling and Melting Points of Some Triglycerides (41)

Triglyceride	Boiling point, °C.		Melting point, °C.
	50 μ	1 μ	
Tributyrin	91	45	
Tricaproin	135	85	
Tricaprylin	179	128	
Tricaprin	213	159	31.5–32.0
Trilaurin	244	188	45.0–46.5
Trimyristin	275	216	56–57
Tripalmitin	298	239	64.5–65.5
Tristearin	313	253	71–72

4. Density, Molar Volume, and Dilation

The density, d , of any substance is the mass per unit volume, dm/dv , where m is the mass and v the volume. Density, which is expressed in grams per cubic centimeter, is sometimes referred to as absolute density to distinguish it from relative density or specific gravity, which is the ratio of the mass of a substance to the mass of an equal volume of water at 4°C. or at some other specified temperature, ordinarily denoted as $d_4^{t_2}$.

Lutskii (42) developed an equation for calculating the density of a compound having n number of carbon atoms. This equation is

$$d_n = d_1 bn / (bn + 1)$$

where d_1 is the limiting density for the given homologous series, and b is a constant. Empirical values of d_1 and b are 0.877 and -4.486 , respectively, for fatty acids at 20°C . Deviations of calculated from experimental densities are claimed not to exceed 0.5%, usually less than 0.25%.

Molar volume is the volume occupied by one mole of a substance, and is derived by dividing the molecular weight by the density of the substance. Specific volume is the reciprocal of the absolute density.

When a substance is heated or cooled, it expands or contracts, i.e., it undergoes a change in volume and, therefore, in density. In the case of liquids, expansion or contraction usually can be expressed as some simple function of the temperature, but in the case of solids the change in volume may be complicated by changes in the crystalline state, i.e., from one polymorphic form to another, and in such cases it is not possible to relate in any simple manner the volume at one temperature to that at another.

The factor that relates the volume of a liquid at one temperature to that at another temperature is known as the *coefficient of volume expansion*, and it is defined as the ratio of the change in volume per degree to the volume at 0°C ., if the substance is liquid at this temperature. The value of the coefficient varies with temperature. The general equation for the magnitude m_t (length or volume) at a temperature t , where m_o is the magnitude at 0°C ., is

$$m_t = m_o (1 + at + bt^2 + ct^3 \dots)$$

where a , b , c , etc., are empirically determined coefficients. The volume expansion of liquids can be expressed as

$$V_t = V_o(1 + bt)$$

The above-mentioned properties and relationships are of considerable utility in their application to the fatty acids and derived products. They have, however, received little systematic attention; such data as are available are in some cases not too useful and others are of questionable accuracy. Although various isolated values for the densities or specific gravities of an appreciable number of the fatty acids and esters can be found in the literature, they are quite often not comparable owing to the different temperatures employed in determining them. Also, in some cases it is not certain whether the value reported refers to density or specific gravity.

(a) Densities and Specific Volumes of Saturated Fatty Acids

A compilation of specific gravities, typical of those found in the literature for the unsaturated fatty acids and methyl and ethyl esters, are given in Table 97.

TABLE 97
Specific Gravities of Normal Fatty Acids and Methyl and Ethyl Esters^a

Acid	Specific gravity	Methyl ester	Ethyl ester
Formic	1.220	0.975	0.906
Acetic	1.049	0.933	0.899
Propionic	0.992	0.917	0.891
Butyric	0.959	0.898	0.879
Valeric	0.942	0.910 ⁰	0.877
Caproic	0.929	0.904 ⁰⁰	0.875 ⁴¹⁵
Heptanoic	0.922	0.881 ⁵¹⁵	0.872 ⁴¹⁵
Caprylic	0.910	0.887	0.878 ¹⁷
Nonanoic	0.907	0.877 ^{17.5}	0.866 ^{17.5}
Capric	0.895 ³⁰		0.862
Lauric	0.883		0.868 ⁴¹³
Myristic	0.858 ⁴⁶⁰		
Palmitic	0.853 ⁴⁶²		
Margaric	0.853 ⁶⁰		
Stearic	0.847 ^{69.3}		
Stearic	0.8358 ⁴⁹⁰		0.8075 ⁴⁹⁰

^a The superscripts refer to the temperatures at which the determinations were made and the subscripts refer to the temperatures of comparison substances; where no sub- and superscripts are given the values are for 20°/4°C.

Garner and Ryder (43) determined the densities and specific volumes of the saturated fatty acids from caprylic to lauric by the so-called air-thermometer method. Two measurements were made for each state, solid and liquid, and from these data the temperature coefficients per degree Centigrade were calculated with the results shown in Table 98. They also determined the densities of the same acids in the liquid state by the pycnometer method at two temperatures, one of which was as close as possible to the melting point. The densities and calculated temperature coefficients for the liquid state are given in Table 99.

Following the work of Garner and Ryder few systematic investigations of the densities of the saturated fatty acids were reported until Dorinson *et al.* (44) determined the densities of the homologous series of acids from caproic to stearic. The determinations were made in a modified Ostwald pycnometer at a temperature of $80 \pm 0.05^\circ\text{C}.$, and all weighings

TABLE 98

Densities, Specific Volumes, and Temperature Coefficients of Fatty Acids from C_8 to C_{12} by the Air Thermometer Method (43)

Acid	Temperature, °C.	Density, g./cc.	Specific volume, 1/d	Temp. coeff. per °C.
Caprylic	10.0	1.0326	0.9685	0.00098
	15	1.0274	0.9733	
	20	0.9109	1.0979	0.00046
	25	0.9090	1.1002	
Nonanoic	5.0	0.9952	1.0048	0.00074
	10	0.9916	1.0085	
	15	0.9097	1.0993	0.00104
	25	0.9011	1.1097	
Capric	15.0	1.0266	0.9741	0.00085
	25	1.0176	0.9827	
	35	0.8927	1.1202	0.00128
	40	0.8876	1.1266	
Hendecanoic	0.12	1.0431	0.9587	0.00054
	10.0	1.0373	0.9640	
	20	0.9948	1.0052	0.00079
	25	0.9905	1.0096	
	30	0.8907	1.1227	0.00093
	35	0.8871	1.1273	
Lauric	35.0	1.0099	0.9902	0.00087
	40	1.0055	0.9945	
	45	0.8767	1.1406	0.00142
	50	0.8713	1.1477	

TABLE 99

Densities and Temperature Coefficients of Fatty Acids from C_8 to C_{12} in the Liquid State by the Pycnometer Method (43)

Acid	Temperature, °C.	Density, g./cc.	Temp. coeff. per °C.
Caprylic	50.27	0.8862	0.00099
	20.02	0.9101	
Nonanoic	50.17	0.8813	0.00097
	15.00	0.9087	
Capric	50.17	0.8773	0.00095
	35.05	0.8884	
Hendecanoic	50.15	0.8741	0.00095
	30.00	0.8889	
Lauric	50.25	0.8707	0.00095
	45.10	0.8744	0.00095

TABLE 100
Densities of Normal Fatty Acids from C₆ to C₁₈ at 80°C. (44)

Acid	Density, g./cc.	Acid	Density, g./cc.
Caproic	0.8751	Tridecanoic	0.8458
Heptanoic	0.8670	Myristic	0.8439
Caprylic	0.8615	Pentadecanoic	0.8423
Nonanoic	0.8570	Palmitic	0.8414
Capric	0.8531	Margaric	0.8396
Hendecanoic	0.8505	Stearic	0.8390
Lauric	0.8477		

were corrected for the buoyancy of air. The values for the densities found by Dorinson *et al.* are given in Table 100. In 1952, the densities of all the even-number carbon acids from C₂ to C₁₈ and their alkyl esters were determined and compared at the same temperature by Gros and Feuge (45), with the results given in Table 101. These authors estimated

TABLE 101
Densities (g./cc.) of Saturated Fatty Acids and Their Methyl
and Ethyl Esters at 75°C. (45)

Carbon Atoms in fatty acid chain	Acid	Methyl ester	Ethyl ester
2	0.8978		0.8320
4	0.9043	0.8359	0.8205
6	0.8796	0.8313	0.8198
8	0.8662	0.8287	0.8191
10	0.8583	0.8271	0.8196
12	0.8516	0.8259	0.8195
14	0.8481	0.8252	0.8197
16	0.8446	0.8247	0.8198
18	0.8431	0.8244	0.8218

that the products used in these determinations were 99% pure or better. For densities of the less common fatty acids, see (45a).

The densities and viscosities of the methyl, propyl, and isopropyl esters of a number of saturated fatty acids were determined by Bonhorst *et al.* (25), with the results indicated in Table 102. Vogel (36) determined the

densities of the alkyl esters of twelve saturated acids with chain length up to C₁₂, and some dibasic acids, using products of good purity. Several selected values reported by Vogel are given in Table 103. The densities of ethyl esters of several saturated acids from C₆ to C₁₈ and of a series of

TABLE 102
Densities and Viscosities of Methyl, Propyl, and Isopropyl
Esters of Fatty Acids (25)

Ester	Density, g./cc.		Viscosity, centistokes	
	20°C.	60°C.	20°C.	60°C.
<i>Methyl</i>				
Caproate	0.8844	0.8460	1.026	0.632
Caprylate	0.8775	0.8420	1.590	0.911
Caprate	0.8730	0.8399	2.437	1.276
Laurate	0.8695	0.8376	3.540	1.732
Myristate	0.8671	0.8361	5.201	2.323
Palmitate		0.8354		2.998
Stearate		0.8363		3.666
<i>Propyl</i>				
Caproate	0.8680	0.8322		
Caprylate	0.8638	0.8305	2.164	1.188
Caprate	0.8620	0.8301	3.241	1.626
Laurate	0.8600	0.8297	4.693	2.206
Myristate	0.8592	0.8295	6.707	2.965
Palmitate		0.8297		3.588
Stearate		0.8296		4.406
<i>Isopropyl</i>				
Caproate	0.8570	0.8200	1.346	0.794
Caprylate	0.8555	0.8210	2.052	1.125
Caprate	0.8543	0.8219	3.081	1.542
Laurate	0.8536	0.8232	4.559	2.113
Myristate	0.8532	0.8233	6.570	2.795
Palmitate		0.8241		3.477
Stearate		0.8244		4.355

alkyl acetates were reported by Shigley *et al.* (29). These authors used modified Sprengle-type pycnometers immersed in baths at temperatures controlled to $\pm 0.05^\circ\text{C}$. The values obtained at five temperatures are listed in Table 104.

TABLE 103
Densities (d_{-4}^{20}) of Alkyl Esters of Mono- and Dicarboxylic Acids (36)

Ester	Methyl	Ethyl	<i>n</i> - Propyl	Iso- propyl	<i>n</i> - Butyl	Iso- butyl	<i>n</i> - Amyl	Iso- amyl
Formate		0.9229	0.9039	0.877	0.8917	0.8798	0.8846	0.8827
Acetate	0.9390	0.9009	0.8867	0.871	0.8813	0.8710	0.8745	0.8719
Propionate	0.9150	0.8917	0.8822		0.8750			
<i>n</i> -Butyrate	0.8981	0.8790	0.8722		0.8692		0.8659	0.8642
Isobutyrate	0.8884	0.8685	0.8643		0.8618			
<i>n</i> -Valerate	0.8895	0.8736	0.8702		0.8680		0.8638	
Isovalerate	0.8807	0.8652	0.8617		0.8608			
Caproate	0.8850	0.8712						
Heptanoate	0.8815	0.8702						
Caprylate	0.8784	0.8693						
Caprate	0.8733	0.8648	0.8623		0.8614			
Laurate	0.8702	0.8618	0.8617		0.8603			
Oxalate ^a		1.0794	1.0186	0.9947	0.9874		0.9662	0.9609
Succinate ^a	1.1198	1.0416	1.0015	0.9847	0.9768	0.9675	0.9598	0.9579
Adipate ^a	1.0625	1.0088	0.9810	0.9659	0.9624		0.9478	0.9454

^a Diesters of the dicarboxylic acids.

TABLE 104
Densities (g./cc.) at Various Temperatures (°C.) (29)

Substance	35°	50°	65°	80°	95°
Ethyl caproate	0.8569	0.8426	0.8284	0.8141	0.7998
Ethyl caprylate	0.8541	0.8410	0.8279	0.8148	0.8017
Ethyl caprate	0.8523	0.8399	0.8275	0.8151	0.8026
Ethyl laurate	0.8506	0.8389	0.8271	0.8153	0.8035
Ethyl myristate	0.8496	0.8383	0.8270	0.8156	0.8042
Ethyl palmitate	0.8489	0.8379	0.8268	0.8158	0.8047
Ethyl stearate	0.8487	0.8378	0.8270	0.8161	0.8053
Hexyl ethanoate	0.8594	0.8454	0.8314	0.8175	0.8036
Octyl ethanoate	0.8558	0.8431	0.8302	0.8174	0.8044
Decyl ethanoate	0.8545	0.8415	0.8293	0.8172	0.8051
Dodecyl ethanoate	0.8520	0.8404	0.8289	0.8173	0.8057
Tetradecyl ethanoate	0.8510	0.8398	0.8286	0.8175	0.8063
Hexadecyl ethanoate	0.8502	0.8393	0.8284	0.8175	0.8066
Octadecyl ethanoate	0.8494	0.8388	0.8282	0.8176	0.8068

(b) Molar Volumes of Saturated Fatty Acids

As previously mentioned, the molar volume of a substance in the liquid state may be ascertained by dividing the molecular weight of the sub-

stance by its density. In the case of the solid state, the molar volume is also related to the cross-section area of the unit cell of the crystal for any given polymorphic form. If, for example, the molar volume in the solid state is known and the length of the unit cell is determined, e.g., by x-ray measurement, then the cross-section area of the unit cell of the crystal can be calculated.

Prior to the work of Garner and Ryder (43) in 1925 no calculations had been made of the molar volumes of the higher aliphatic acids in the solid

TABLE 105
Molar Volumes (cc./g. mole) of Fatty Acids in Solid and Liquid States

Acid	Liquid			Solid (at 15°C.)	
	Pauly (46) ^a	Garner and Ryder (43) ^b	Incre- ment	Garner and Ryder (43)	Incre- ment
Formic	41.2		22.6		
Acetic	63.8		22.0		
Propionic	85.8		22.4		
Butyric	108.2		21.7		
Valeric	129.9		22.7		
Caproic	152.6		21.6		
Heptanoic	174.2		23.4		
Caprylic	197.6	162.61	16.8	140.2	19.9
Nonanoic		179.43	16.8	160.1	17.7
Capric		196.20	16.8	167.8	18.7
Hendecanoic, α -form		212.95		186.5	18.7
Hendecanoic, β -form				180.0	15.2
Lauric		229.84		195.2	

^a Temperature not specified.

^b At 50°C.

state and data for the acids in the liquid state were far from complete, as indicated by the compilation of Pauly (46). Garner and Ryder calculated the molar volumes of the fatty acids from caprylic to lauric in the solid state at 15°C. and in the liquid state at 50°C. Their results, together with those previously reported by Pauly, are given in Table 105.

According to the data of Pauly, the molar volumes of the lower members of the series increase by an average of 22.3 cc. per gram mole in the liquid state for each CH₂ group added to the chain; Garner and Ryder found this increment to be 16.8 cc. per gram mole in the liquid state. In 1950, Joliet (47) reported that he had found the increase in molar volume on the addition of a CH₂ group to a normal fatty acid to be 16.4 ml. at 20°C.

Garner and Ryder observed that in the solid state alternation occurred as the series was ascended. On the basis of the data for this state and the values for the chain length obtained by x-ray measurements, they calculated the cross section of a single molecule in the crystal to be 23.8 Å. This cross section was found to be a nonalternating property, therefore changes in molecular volume must be due entirely to changes in chain length.

Using the values for the densities of the fatty acids given in Table 100 and additional values found in the literature, Dorinson *et al.* (44) calculated, by means of an empirical equation, the molar volumes at 20° and 80°C. for the normal fatty acids from formic to stearic. The calculations were predicated on the fact that the densities of the saturated fatty acids are linear functions of the temperature. These authors found that at 20°C. the molar volumes of the acids from acetic to pelargonic (nonanoic) could be expressed by the equation $V_m = 16.89n + 23.62$, where n is the number of carbon atoms in the chain; at 80°C. the molar volumes of the acids from butyric to stearic could be expressed by the equation $V_m = 17.25 + 28.88$. Only the first three acids of the series deviated appreciably from linearity as expressed by the latter equation.

Hammond and Lundberg (48) developed a general equation for molar volume and density as follows:

$$V_m = M/d = k_4C + k_5D + k_6$$

where M is the molecular weight, d is the density, and k_4 , k_5 , and k_6 are constants. Using this equation, they calculated the molar volumes of the methyl esters of fourteen saturated acids of the series C₁ to C₂₀.

The calculated and experimental values for the molar volumes of the

saturated fatty acids according to Dorinson *et al.*, and the calculated values for the methyl esters of these acids according to Hammond and Lundberg, are given in Table 106.

TABLE 106
Molar Volumes (cc./g. mole) of Saturated Fatty Acids (44) and
Their Methyl Esters (48)

Acid	Fatty acids				Methyl esters
	V_m at 20°C.		V_m at 80°C.		V_m at 20°C., calcd.
	Exptl.	Calcd.	Exptl.	Calcd.	
Formic	37.71	40.51			64.53
Acetic	57.21	57.40	61.11	63.38	81.07
Propionic	74.55	74.29	79.68	80.63	97.61
Butyric	91.93	91.18	97.95	97.88	114.15
Valeric	108.69	108.07	115.33	115.13	130.69
Caproic	125.04	124.96	132.67	132.38	147.23
Heptanoic	141.89	141.85	150.07	149.63	
Caprylic	158.57	158.74	167.30	166.88	180.31
Nonanoic	174.53	175.63	184.50	184.13	196.85
Capric			201.80	201.38	213.39
Undecanoic			218.90	218.63	
Lauric			236.29	235.88	246.47
Tridecanoic			253.27	253.13	
Myristic			270.41	270.38	279.55
Pentadecanoic			287.61	287.63	
Palmitic			304.56	304.88	312.63
Margaric			321.90	322.13	
Stearic			338.85	339.38	345.71
Arachidic					378.79

(c) *Specific Gravities, Densities, and Molar Volumes
of Unsaturated Acids and Esters*

As with many other properties of the unsaturated fatty acids, few data are available with respect to the specific gravity, density, and molar volume of these compounds. Values for the specific gravity of a few unsaturated acids and esters are assembled in Table 107.

The most extensive and painstaking investigation of the densities of oleic acid and its methyl, ethyl, propyl, and butyl esters was made by Keffler and McLean (49). Highly purified oleic acid and alcohols were

TABLE 107
Specific Gravities of Some Unsaturated Acids and Esters^a

Acid		Methyl ester	Ethyl ester
Petroselinic	0.868 ⁴⁰		
Oleic	0.895 ^{17.7}		
Erucic	0.860 ₄ ^{57.1}	0.870	0.865
Linoleic	0.903		0.8846 ₄ ^{15.4} , 0.8776 ₄ ²⁵
Linolenic	0.914		0.8959 ₄ ^{15.4} , 0.8890 ₄ ²⁵

^a The superscripts refer to the temperatures at which the determinations were made and the subscripts refer to the temperatures of comparison substances; where no sub- and superscripts are given the values are for 20°/4° C.

used in the preparation of the esters and measurements were made over a temperature range from 15° to 90°C., as indicated in Table 108. On the basis of the values of the densities for the temperature range 30° to 90°C.,

TABLE 108
Densities of Oleic Acid and Alkyl Oleates (49)

Temperature, °C.	Oleic acid	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate
15	0.8939	0.8774	0.8724	0.8708	0.8704
20	0.8905	0.8738	0.8687	0.8673	0.8669
25	0.8870	0.8702	0.8651	0.8637	0.8634
30	0.8835	0.8666	0.8613	0.8601	0.8599
60	0.8634	0.8450	0.8400	0.8389	0.8390
90	0.8429	0.8234	0.8183	0.8175	0.8178

the calculated temperature coefficients of density were found to be: oleic acid, 0.00068; methyl oleate, 0.00072; propyl oleate, 0.00071; and butyl oleate, 0.00070.

Keffler and McLean, using the density values in Table 108, calculated the molar volumes and increments in molar volume of oleic acid and the alkyl oleates, corresponding to temperatures of 30°, 60°, and 90°C. as shown in Table 109.

TABLE 109
Molar Volumes and Increments in Molar Volumes for
Oleic Acid and Alkyl Oleates (49)

Compound	Molar volume at 30°C.	Incre- ment	Molar volume at 60°C.	Incre- ment	Molar volume at 90°C.	Incre- ment
Oleic acid	319.5		326.9		334.9	
		22.4		23.7		24.9
Methyl oleate	341.9		350.6		359.8	
		18.4		18.8		19.4
Ethyl oleate	360.3		369.4		379.2	
		16.8		17.2		17.5
Propyl oleate	377.1		386.6		396.7	
		16.4		16.7		17.0
Butyl oleate	393.5		403.3		413.7	

Hoerr and Harwood (50) calculated the molar volumes of highly purified oleic and linoleic acids to be 318 and 321 cc./mole at 20°C., respectively, compared to 297 cc./mole at the same temperature for the calculated molar volume for stearic acid.

Sims (51) reported the densities of a few esters of unsaturated acids which were determined by the falling drop method. The densities, determined to within ± 0.003 ml./g. at $25 \pm 0.002^\circ\text{C}$., are given in Table 110.

TABLE 110
Densities of Some Esters at 25°C. (51)

Material	Density, g./cc.
Triolein	0.9117
Methyl eicosenoate	0.8706
Methyl oleate	0.8720
Methyl erucate	0.8764
Methyl linoleate	0.8861
Methyl linolenate	0.8957

The diglycerides of edible, fat-forming acids were acetylated with dibasic acids by Feuge and Ward (51a), purified, and their densities and other properties determined, as given in Table 110a.

Optically active diglycerides were prepared by Baer and Buchnea (51b) and determined to be of assured structural and optical purity. In order to prepare *d,l*-1,2-diolein, they synthesized *d,l*-1,2-(bis-9,10-*cis*-dibromo) distearins, the first diglycerides of established structure and configuration

TABLE 110a
Characteristics of Diglyceride Esters of Dibasic Acids (51a)

Diglyceride ester	M.p., °C.	n_D^{25}	Density, g./cc.			Kinematic viscosity, centistokes	
			30°C.	50°C.	70.2°C.	38.8°C.	98.8°C.
Diolein							
fumarate		1.44900	0.9458	0.9346	0.9277	86.50	13.60
succinate		1.44709	0.9384	0.9281	0.9206	77.00	13.00
adipate		1.44671	0.9397	0.9310	0.9230	116.70	21.27
Diolein	21.5	1.44408					
			94.6° C.	107.2° C.	123° C.		
Distearin							
fumarate	83.1	1.43851	0.9074	0.9008	0.8927	solid	20.64
succinate	89.8	1.43861	0.8682	0.8641	0.8583	solid	17.87
adipate	82.1	1.43844	0.8910	0.8831	0.8731	solid	18.93
Distearin	78.2	1.43583					

containing halo fatty acids. Refractive indices of the *d,l*-diglycerides were identical (n_D^{25} , 1.4679), as were the densities (d_4^{20} , 0.9218); likewise, the *d,l*-halodiglyceride (n_D^{23} , 1.4996, and d_4^{20} , 1.2335).

(d) *Dilation of Fatty Acids and Esters*

As has been previously mentioned, all substances undergo a change in volume of heating, the magnitude of which can be determined from measurements of the density of the substance at various temperatures. It is difficult and, in many cases, impossible to follow changes in density by direct measurement over a wide range of temperatures, but such changes can be determined with comparative ease and simplicity by means of the dilatometer. Furthermore, the use of a dilatometer permits continuous observation or measurement of the change in volume of a substance in both the solid and liquid states, and, in addition, reveals other useful information, such as changes from one polymorphic form to another and from solid to liquid. The melting point can be determined very accurately by use of the dilatometer and in the case of fats is the only method by which this can be done with a high degree of accuracy.

In principle the dilatometer is not unlike a thermometer and consists essentially of a reservoir, which is filled with the substance whose change in volume it is desired to measure and a confining liquid, attached to a

U-shaped capillary graduated or otherwise provided with a means of observing the change of volume as a function of change in temperature of the system.

Various types of dilatometers and the methods of applying them in investigations of fatty acids and natural fats have been described by Normann (52), van Roon (53), Jensen (54), Reinders, Doppler, and

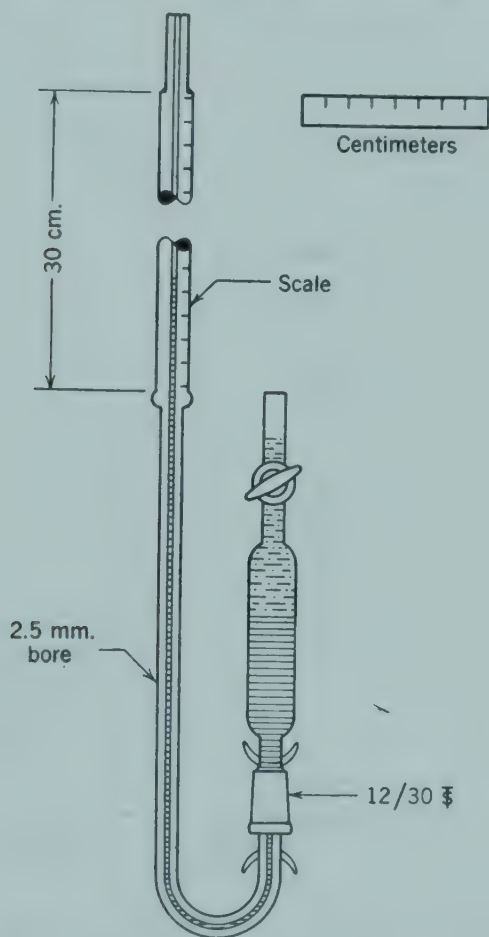


Fig. 35. Type A or volumetric type of dilatometer (58).

Oberg (55), Coffey and Spannuth (56), Hofgaard (57), Bailey and co-workers (58-61), and others.

The Dilatometer. The dilatometers described by Bailey and Kraemer represent improvements in construction over those used by Normann, Hofgaard, and others, and they are described here in preference to older types. The dilatometers of Bailey and Kraemer are of two types, the constructions of which are illustrated in Figures 35 and 36.

Type A (Fig. 35) is of the usual volumetric variety, not essentially different from that first described by Normann. Its novel features consist of the introduction of a ground-glass joint between the bulb and the side arm, to facilitate filling and cleaning, and the provision of a scale of new design. The scale is made from a section of a 50-ml. burette, and is attached permanently to the side arm. The capillary must of course be

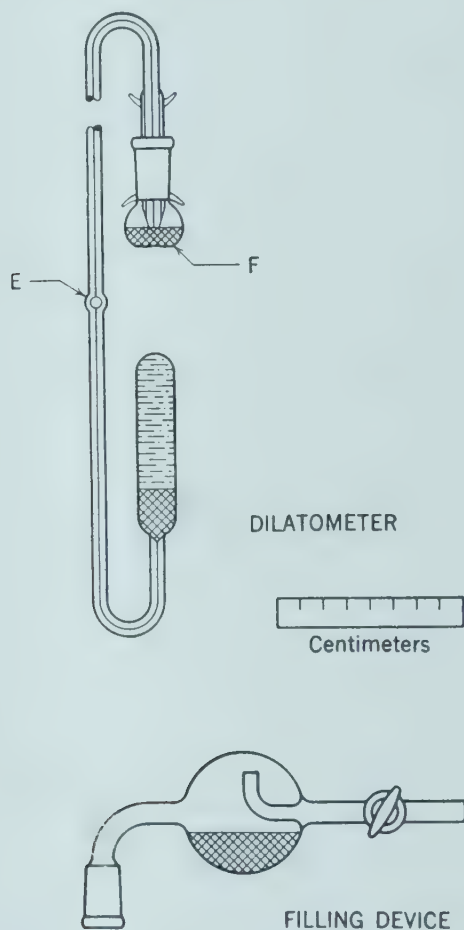


Fig. 36. Dilatometer and filling device—type B or gravimetric type (58).

calibrated. In this dilatometer water is usually employed as the confining liquid, although mercury may also be used. It is useful chiefly for the examination of fats of relatively low melting points, in cases where extreme accuracy in the measurements is not required.

In filling this dilatometer, complete displacement of air is effected by permitting the confining fluid to enter through the side arm and force a

small portion of the sample out through the stopcock. The weight of the fat actually retained in this bulb is determined at the conclusion of the experiment by washing out the interior of the bulb through the ground-glass joint, weighing the bulb plus the fat retained in the outlet tube and stopcock bore, and subtracting the weight of this fat from the weight of the original sample. The weight of the confining fluid must also be determined, so that the total observed expansion can be properly distributed between sample and confining fluid.

Dilatometer *B* (Fig. 36) is of the gravimetric type, and may be considered a modification of the instrument described by Burlew (62). In this dilatometer mercury is used as the confining liquid; the mercury thread in the capillary side arm communicates with a reservoir or mercury in the small flask, *F*. Volume changes in the fat cause mercury to be expelled into the reservoir or withdrawn therefrom. Readings are made by detaching and weighing the flask and its contents. In the event of formation of an air bubble in the capillary as a result of detaching the flask for weighing, the bubble may be eliminated by raising the dilatometer from the bath a sufficient distance to expose expansion bulb *E*, and by gently warming the bulb.

After the sample is placed in the bulb, the side arm is sealed on by fusion. The filling device illustrated in Figure 35 is provided for filling the dilatometer with mercury. The dilatometer containing the sample is connected to the filling device by means of the ground-glass joint provided for the purpose, and the sample is melted and degassed under vacuum. The assembly of dilatometer and filling device is then tilted to bring the mercury in the latter over the tip of the capillary, and the stopcock is turned to shut off the vacuum and admit air which forces mercury into the dilatometer. Manipulation of the assembly is simplified if the fat is chilled until pasty before the mercury is admitted to the system. A high vacuum should be employed, to eliminate completely air bubbles in the bulb.

Before the reservoir flask is attached, lubricant should be removed from the male joint on the end of the capillary, to ensure constant weight of the flask and to permit the joint to pass sufficient air to avoid building up pressure in the flask as the mercury expands.

This latter type of dilatometer is recommended for all precise work, and particularly for use with highly saturated fats, which must be carried to relatively high temperatures, and which are inclined to undergo very slow polymorphic transformations. Since the instrument is sealed to form one solid, all-glass apparatus the possibility of leakage is eliminated.

Ordinarily mercury can be weighed with greater accuracy than its volume can be measured; hence smaller volume changes can be detected with this dilatometer than with those of the usual type. The use of mercury as the confining fluid eliminates slight inaccuracies due to the appreciable solubility of water in fats.

Method of Determining the Expansion of Fatty Acids. The dilatometer has found increasing application in the investigation of fats and fat products, especially since about 1940, but it has not found extensive application in the examination of the fatty acids and scarcely any in the case of the monoesters. Normann appears to be one of the first to apply dilatometry to the investigation of the expansibility of fats and oils and their derived fatty acids. He used a simple type of dilatometer consisting of a calibrated cylinder of approximately 15 ml. capacity, closed with a ground-glass stopper, and having attached at the lowest point a vertical, graduated capillary side arm which was closed at the upper end with a rubber bulb from a dropping bottle.

In using the dilatometer in investigating the expansibility of fatty acids it was weighed, filled with boiled water to the desired point, i.e., to a point one-third to two-thirds the height of the anticipated maximum expansion, and then weighed again. It was then warmed and while warm it was filled with melted, air-free fatty acid, and then closed, cooled, and weighed again. The filled dilatometer was placed in a thermostatically controlled water bath and allowed to remain 15 to 20 minutes, after which the temperature and height of the water in the capillary were read. The temperature of the bath was raised by increments, and after 20 minutes the temperature and capillary height were again recorded. This sequence of operations was repeated throughout the desired temperature range, and up to approximately 10°C. above the melting point of the fatty acids.

The calculations were made from the known weights of the dilatometer, water, and fat. Since the expansion of water per gram per degree rise in temperature was known, the total expansion of the contents of the dilatometer was read on the graduated capillary, and from these data the expansion due to the fatty acid was calculated. From these values the expansions per gram, or per one hundred grams of fatty acid were calculated and the results plotted in the form of graphs. As pointed out by Normann, these values represent apparent expansions in glass and are related to the original volume rather than the original weight of the fatty acid. By making use of the specific gravity of the acid, the specific vol-

ume expansions could be calculated, but these too are apparent values in glass and not absolute values.

Normann determined the expansibility over a limited temperature range and the melting dilation of stearic and elaidic acids by the method and apparatus just described. The results are reproduced in Table 111 and graphically in Figure 37.

TABLE 111
Relative Expansions of Stearic and Elaidic Acids by the
Normann Dilatometer Method (52)

Stearic acid (m.p. 68–70°C.)		Elaidic acid (m.p. 44°C.)	
Temperature, °C.	Relative expansion	Temperature, °C.	Relative expansion
48.2		16.9	
52.3	465	20.7	0.0
57.3	1155	27.5	54
59.8	1455	32.7	181
62.2	1956	37.2	435
64.4	3100	41.0	1030
67.3	3705	43.9	6490
71.8	15450	46.4	15540
75.3	16650	49.0	15800
78.1	17280	52.2	16150
81.2	17550	55.6	16500
		60.0	16950

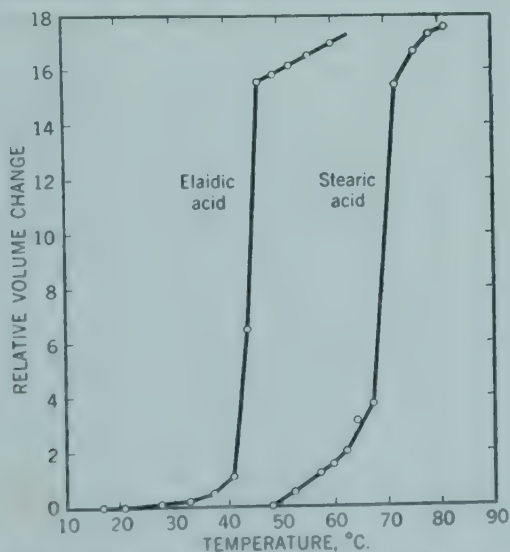


Fig. 37. Expansibility and melting dilation of stearic and elaidic acids according to Normann (52).

It is evident from the curves in Figure 37 that the melting point of the sample of elaidic acid used by Normann is relatively sharp while that of the stearic acid is anything but sharp, thus indicating the effect of impurities in the commercial acid used in making these measurements. Also, it may be noted that the expansion of elaidic acid between 17 and 30°C. is practically zero which is probably due to the balancing of two thermal changes.

Normann also determined the expansion of oleic acid over a series of temperature ranges, namely, 20 to 72°C., 0 to 77°, -21 to 81°, and -12 to 39.0°. When these data were plotted in graphic form, it was found that all of the curves were parallel above 20°C. but below this temperature the various samples appeared to behave anomalously and it was, therefore, concluded that the oleic acid used was impure. Although the sample of oleic acid was probably impure, as stated by Normann, nevertheless part of the apparent anomaly was due in the lower temperature region to unrecognized transitions from one polymorphic form to another. It is now known (57-61) that the prior history of the sample is an all-important consideration in interpreting the results of dilatometric measurements. Normann recognized this to some extent in the observation that the original temperature in the solid state affected the subsequent expansion, and he recommended that, in the examination of commercial fats, they all be brought to an arbitrary minimum temperature of 20°C. However, this temperature is well above many of the transitions occurring in various fats, fatty acids, and fatty acid derivatives, consequently these materials must be cooled to relatively low temperatures and tempered to produce the most stable modification.

Gravimetric dilatometry has been employed to determine the expansibility characteristics of only a few fatty acids. Singleton *et al.* (63,64) used this method to determine the expansibility characteristics of stearic and palmitic acids. Stearic acid was obtained in the two forms corresponding to the B- and C-spacings; palmitic in the highest melting form. Expansibility of these two acids in the solid and liquid states, and melting dilations are given in Table 112.

Singleton and Ward (65) applied the dilatometric method to determine the effect of positional and geometric isomerism in two pairs of octadecenoic acids with respect to expansibility, melting dilation and density, with the results given in Table 113. The two pairs of octadecenoic acids were normal oleic and its *trans*-isomer elaidic, and normal petroselenic and its *trans*-isomer petroselaidic. In the liquid state, the absolute specific volumes of the four acids were very nearly equal, whereas at tem-

TABLE 112
Expansibility and Melting Dilation of Stearic and Palmitic
Acids in the Solid and Liquid States (63,64)

Acid	State	Spacing	Temperature range, °C.	Expansion ml./g./°C.	Average expansion ml./g./°C.	Melting dilation ml./g.
Stearic	Solid	C	-20.88 to +18.42	0.000258		
	Solid	C	-20.88 to +18.42	0.000274		0.1857 ^a
	Solid	C	-38.59 to + 6.02	0.000255	0.000262	
	Solid	B	-20.88 to +30.41	0.000275		0.2051
	Solid	B	-38.59 to +28.87	0.000263	0.000269	0.2045
	Liquid	C	70.00 to 76.18	0.000953		
	Liquid	C	70.00 to 76.18	0.000990		
	Liquid	C	71.85 to 76.05	0.000965		
	Liquid	C	71.85 to 76.05	0.000957		
	Liquid	C	70.00 to 76.18	0.000998	0.000973	
	Liquid	C	70.00 to 76.18	0.000998	0.000973	
Palmitic	Solid		- 7.00 to +40.00	0.000280		0.1806
	Liquid		62.90 to 72.00	0.000968		

^a Calculated from the specific volume of the B-form after transition to the C-form of stearic acid.

TABLE 113
Expansibility and Melting Dilation of Four Octadecenoic Acids (65)

Acid	Expansibility, ml./g./°C.		Melting dilation, ml./g.	Specific volume	
	Solid state	Liquid state		ml./g.	Temp., °C.
Oleic (<i>cis</i>)	0.000269 ^a	0.000957	0.1183	1.1230	20.0
	0.000308 ^b				
Petroselinic (<i>cis</i>)	0.000369	0.000895	0.1314	1.1442	45.0
Elaidic (<i>trans</i>)	0.000253	0.000968	0.1615	1.1555	55.0
Petroselaidic (<i>trans</i>)	0.000308	0.000900	0.1403	1.1537	55.0

^a Below -5° C.

^b Between -4° and 10°C.

peratures below -7°C. at which all were in the solid state, the specific volumes of petroselinic and elaidic acids were at variance with the specific volumes of oleic and petroselaidic acids. This variance is attributed to differences in crystal packing.

The melting dilations of the *trans*-isomers were found to be greater than that of the *cis*-isomer. Of the two *cis*-isomers, the melting dilation is less for that isomer in which the double bond is farthest removed from the carboxyl group.

The methyl esters of palmitic, stearic, arachidic, behenic, and oleic acids were investigated by Craig (66) and their expansibilities found to be as given in Table 114. The temperature interval used by Craig to cal-

TABLE 114
Melting Dilation and Expansibility of Some Methyl Esters (66)

Methyl ester	Expansibility, ml./g./°C.		Melting dilation	
	Solid state	Liquid state	ml./g.	ml./mole
Palmitate	0.00025	0.00099	0.1698	45.92
Stearate	0.00022	0.00100	0.1726	51.52
Arachidate	0.00025	0.00101	0.1769	57.76
Behenate	0.00022	0.00100	0.1821	64.57
Oleate	0.00036 ^a	0.00090	0.1187	35.19

^a Between -38° and -25° C.

culate the expansibilities in the solid state was -38 to -20°C. The coefficient 0.00030 ml./g./°C. was used to calculate the melting dilation of methyl oleate.

The dilation of several of the glyceryl esters of fatty acids have been reported. For example, Singleton and Vicknair (67) determined the expansibility of monostearin in its four established polymorphic forms, and calculated the volume changes associated with the melting dilation of each form. For these calculations the value used for the absolute density of monostearin was 0.9039 g./ml. at 85°C., determined by the pycnometer method. Data for the expansibility of monostearin are given in Table 115. Expansibility of the liquid monostearin was found to be 0.000920 ml./g./°C.

TABLE 115
Expansibility in the Solid State, Specific Volume, and Melting Dilation of the β -, β' -, and Sub- α - Forms of 1-Monostearin (67)

Form	Expansibility in solid state, ^a ml./g./°C.	Specific volume, ^b ml./g.	Melting dilation, ml./g.
β	0.000241	0.9419	0.1367
β'	0.000291	1.0307	0.0610
Sub- α	0.000303	0.9515	0.1292

^a -38° to +12°C.

^b At -38.86°C.

A comparison of the melting dilations of the stable forms of stearic acid and tristearin with the corresponding determination for monostearin revealed an interesting relationship. The melting dilations of stearic acid, tristearin, and monostearin are 0.1857 (60), 0.1671 (63), and 0.1367 ml./g. (67), respectively. On a weight basis, the content of stearyl ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}-$) groups in tristearin is 90.0% and in monostearin it is 74.6%. Multiplying the melting dilation of stearic acid by the content of stearyl of tristearin and monostearin yields values for the melting dilation of tristearin and monostearin of 0.1671 and 0.1385 ml./g., respectively. The observed and calculated melting dilations of tristearin are seen to be identical, whereas they differ only 1.4% for monostearin, which could be due to experimental error in determining the melting dilation. The melting dilations of these products are in direct proportion to the mole percentage of stearyl groups present in each compound.

The melting dilation of a number of saturated *n*-fatty acids and their mono- and diglycerides were investigated by Singleton and Gros (68). The relationship between fatty acids and their glyceryl esters with respect to melting dilation were calculated, with the results given in Table 116.

TABLE 116
Expansibilities and Melting Dilations of Some Fatty Acids
and Their Glyceryl Esters (68)

Material	Expansibility, ml./g./°C.		Melting dilation			
			Observed		Calculated	
	Solid	Liquid	ml./g.	ml./mole	ml./g.	ml./mole
Stearic acid	0.00026	0.00097	0.186	52.9	0.186	52.9
Monostearin	0.00024	0.00092	0.137	49.1	0.139	49.8
Tristearin	0.00023	0.00092	0.167	148.9	0.167	148.9
Palmitic Acid	0.00028	0.00097	0.181	46.4	0.182	46.7
Tripalmitin	0.00022	0.00092	0.162	130.8	0.162	130.0
Myristic acid					0.173	39.5
Monomyristin	0.000345	0.000844	0.118	35.7	0.121	36.6
Dimyristin	0.000435	0.00100	0.141	72.3	0.143	73.3
Trimyristin	0.00021	0.00091	0.152	109.9	0.152	109.9
Lauric acid					0.166	33.2
Monolaurin	0.000341	0.000956	0.110	30.2	0.111	30.5
Dilaurin	0.000391	0.000874	0.126	57.5	0.133	60.7
Trilaurin	0.00019	0.00090	0.143	91.5	0.143	91.5
Capric acid	0.000329	0.000984	0.124	21.4	0.124	21.4
Monocaprylin	0.000204	0.000736	0.052	11.3	0.052	11.3
Caproic acid	0.00035	0.00098	0.116	13.5	0.116	13.5
Monoolein	0.00034	0.00081	0.067	24.0	0.067	24.0

A comparison of the observed melting dilations on a mole basis, of the mono-, di-, and triglycerides of each fatty acid revealed that the melting dilation of the monoglyceride is one-half that of the diglyceride and one-third that of the triglyceride. This relationship indicates that the end methyl group of the glyceryl esters contributes approximately the same effect to the melting dilation of these compounds, and that the increment in volume change is regular with the addition of each two methylene groups, which is analogous to the relationship between chain length and certain thermal properties observed by Garner *et al.* (69) in the homologous series of saturated fatty acids.

Equations were developed to express, on a gram-mole basis, the melting dilation (ΔV) of a mono-, di-, or triglyceride of any even-numbered, saturated *n*-fatty acid having a chain length greater than ten carbon atoms. These equations are as follows:

$$\begin{array}{ll} \text{Monoglycerides} & \Delta V = (n - 2)a + b \\ \text{Diglycerides} & \Delta V = 2[(n - 2)a + b] \\ \text{Triglycerides} & \Delta V = 3[(n - 2)a + b] \end{array}$$

where *a* and *b* are constants equal to 3.24 and -2.08 , respectively; and *n* is the number of carbon atoms in the acyl group.

A similar equation was developed to express the melting dilations of the corresponding saturated fatty acids which is as follows:

$$\Delta V = (n - 2)a + b$$

where *n* has the same significance as above and the values of *a* and *b* are 3.47 and -3.24 , respectively.

The melting dilation per acyl radical for each type of glyceride is approximately 3 ml./mole less than the melting dilation of the corresponding fatty acid.

The expansibilities of the saturated triglycerides from trilaurin through tristearin, and of triolein and trielaidin were determined by Bailey and Singleton (60) using gravimetric dilatometers, with the results given in Table 117. These authors also calculated the volume changes (contraction) for the transitions from one polymorphic form to another for the three forms of tristearin, which are as follows:

Form III to II:	0.0061 ml./g.
Form III to I:	0.0354 ml./g.
Form II to I:	0.0299 ml./g.

TABLE 117
Expansibility and Melting Dilation of Triglycerides (60)

Glyceride	State	Temperature range, °C.	Expansion, ml./g./°C.	Melting dilation, ml./g.	Melting point, °C. ^a
Trilaurin	Solid	-38 to -24	0.00019	0.1428	46.5
	Liquid	47 to 60	0.00090		
Trimyristin	Solid	-38 to -22	0.00021	0.1523	56.6
	Liquid	57 to 66	0.00091		
Tripalmitin	Solid	-38 to -18	0.00022	0.1619	65.5
	Liquid	66 to 76	0.00092		
Tristearin (I)	Solid	-38 to -20	0.00023	0.1671 (I)	72.5 (I)
	(II) Solid	-38 to -33	0.00029	0.1316 (II)	64.5 (II)
	(III) Solid	-38 to -32	0.00032	0.1192 (III)	54.5 (III)
	Liquid	73 to 80	0.00092		
Trielaidin	Solid	-33 to -22	0.00018	0.118	42.0
	Liquid	55 to 62	0.00087		
Triolein	Solid	-38 to -33	<0.00038	0.083	4.6
	Liquid	18 to 27	0.00082		

^a Temperature at which melting dilation was calculated.

From the values of the expansibilities, it can be calculated that the specific volume of the triglycerides listed in Table 117 decrease as their molecular weights decrease, in both solid and liquid states. In the solid state, however, the expansibilities of the triglycerides increase with increasing molecular weight.

Craig *et al.* (70) determined the coefficient of expansion of some pure simple and mixed triglycerides. A gravimetric type of dilatometer was used, similar to that described by Bailey and Kraemer (58) except that the sample tube was joined to the stem by means of a ground joint.

The average values obtained by these workers for the coefficients of expansion of the solid and liquid states and the melting dilations of the various triglycerides are given in Table 118.

All measurements were begun from a temperature base of -10° or -15°C . They found the coefficients of expansion to be nearly the same for all the triglycerides in the liquid state, but in the solid state the saturated triglycerides had lower coefficients of expansion than the unsaturated ones. The melting dilation was found to decrease proportionally to the increase in the number of oleyl groups in the triglycerides.

Craig (70a) established the standard errors in dilatometric measurements for the solid state of methyl stearate. The specific volumes at any temperature in the solid region were found to depend on the previous

TABLE 118
Melting Dilations and Coefficients of Expansion of Triglycerides^a

Material	Melting dilation, ml./g.		Coefficient of expansion, ml./g./°C.			
			Solid state		Liquid state	
	Found	Re-ported	Found	Re-ported	Found	Re-ported ^b
Triolein ^a	0.0597	0.0830	0.00071	0.00038	0.00093	
Triolein ^b	0.0665	0.0830	0.00100	0.00038	0.00099	
Stearodiolein	0.0905		0.00118		0.00105	
Oleodistearin	0.0925		0.00060		0.00092	
Oleodipalmitin	0.0965		0.00053		0.00091	
Palmitodistearin	0.1406		0.00032		0.00093	
			0.00043			
Stearodipalmitin	0.1460		0.00033		0.00097	
			0.00047			
Tristearin	0.1516	0.1671	0.00034	0.00023	0.00095	0.00092
			0.00044			
Tripalmitin	0.1621	0.1619	0.00031	0.00022	0.00097	0.00092
			0.00044			

^a B. M. Craig, W. O. Lundberg, and W. F. Geddes, *J. Am. Oil Chemists' Soc.*, **29**, 128-133 (1952).

^b E. A. Kraemer and A. E. Bailey, *Oil & Soap*, **21**, 254 (1944).

history of the sample, even though not melted between determinations. A continual reduction in specific volume for successive runs was found, which did not affect the coefficient of expansion of the solid state, but increased the melting dilation. The use of Vycor glass dilatometers, and a solidification procedure involving preliminary deaeration of sample, further evacuation of air from the sample after placing in the dilatometer bulb, and slow solidification of the sample from the mercury surface upwards to decrease the possibility of crevices in the solid sample, resulted in improvements in technique. The specific volumes of methyl stearate, as reported by Craig, are given in Tables 118a and 118b.

Gros and Feuge (70b) determined the physical properties of six oleoglycerides, including expansibility and melting dilation. Table 118c gives the results reported. These investigators found that substitution of short-chain acyl groups for one or both of the hydroxyl groups in 1-monoolein increased the density, and lowered the refractive index.

Dilatometry has found widespread use in controlling the hydrogenation (hardening) of fats. The dilatometers employed for this purpose are

TABLE 118a
Specific Volumes of Methyl Stearate for Heating and Cooling Cycles (70a)

Tempera- ture, °C.	Cooling cycles, °C.					Heating cycles, °C.				
	+35 to -38°	+7 to -38°	-14 to -38°	+35 to -11°	+35 to +10°	+10 to +35°	-11 to +35°	-38 to -14°	-38 to +7°	-38 to +35°
-38	0.9821	0.9819	0.9821					0.9819	0.9821	0.9821
-23	0.9840	0.9842	0.9844					0.9848	0.9848	0.9848
-14	0.9853	0.9859	0.9862					0.9862	0.9862	0.9862
-11	0.9858	0.9862		0.9857			0.9857		0.9869	0.9869
-2	0.9873	0.9879		0.9873			0.9877		0.9885	0.9885
+10	0.9898			0.9892	0.9891	0.9891	0.9901			0.9912
+25	0.9938			0.9938	0.9933	0.9943	0.9953			0.9963
+35	0.9988			0.9984	0.9985	0.9985	0.9985			0.9986

TABLE 118b
Variations of Melting Dilations with Specific Volumes
of Solid State at Different Times (70b)

	Specific volume at -38°C., ml./g.	Coefficient of expansion of solid ml./g. $\times 10^{-3}$	Melting dilation	Specific volume at 39.1°C. ^a , ml./g.
April	0.9850	184	0.1740	1.1719
May	0.9837	186	0.1757	
June	0.9829	187	0.1761	
July	0.9821	171	0.1779	

^a Calculated from liquidus line 42 to 58°C.

usually of the volumetric type, such as that described by Fulton *et al.* (71).

5. Viscosity

According to Bridgman viscosity is perhaps the most significant *non*-thermodynamic property of a liquid, and this is certainly true of the fatty acids, esters, and natural fats. This property is especially important wherever movement through or by these substances occurs in the liquid state.

A liquid offers no permanent resistance to forces tending to change its shape, yielding steadily to the slightest deforming force. However, different liquids yield at different rates or offer different resistances to deformation.

This resistance is termed *internal friction* or *viscosity*. Some liquids, like glycerol or oleic acid, flow much more slowly down an inclined plane or tube than does water. Such flow consists in a continuous change in shape of each part of the liquid.

In flow down an inclined plane, the motion is greater near the surface than at the bottom; hence a shearing stress is created; and the ratio of this shearing stress to the rate of shear is a constant for a given liquid, but differs for different liquids. The constant ratio of the shearing stress in a liquid to its rate of shear is called the *coefficient of viscosity*. In other words, if a fluid is flowing in a plane *ab* with a velocity *v*, it exerts on an adjacent plane a tangential drag equal to $\eta(dv/dx)$ per unit of area. η is called the *viscosity*, *coefficient of viscosity*, or *coefficient of internal friction*.

TABLE 118c. Physical Data of Oleoglycerides (70b)

Oleoglyceride	Refractive index n_D^{25}	Density at 35°C., g./ml.	Temperature interval, °C.	Polymorphic form	Coefficient of expansion, ml./g./°C.	Melting dilation, ml./g.	Dilatometric melting point, °C.
1,2-Diaceto-3-olein	1.45180	0.9623	-30 to -21 -38.6 to -30 -17.2 to 50	I II liquid	0.002065 0.000286 0.000912	0.0524	-17.2
1,2-Dibutyro-3-olein	1.45119	0.9438	-37 to -29 -28.3 to 50	I liquid	0.002300 0.000839	0.0233	-28.3
1-Aceto-3-olein	1.45801	0.9536	-38.6 to -15 -13.0 to -5 -29.0 to -13 -38.6 to -30 8.3 to 50	I II ^b III IV liquid	0.000288 0.001080 0.000534 0.000566 0.000863	0.0825 0.0523	8.3 6.8
1-Butyro-3-olein	1.45713	0.9416	-38.6 to -25 -22.5 to -13 -30.0 to -22.5 -38.6 to -31 -3.4 to 50	I II ^b III IV liquid	0.000288 0.001576 0.000553 0.000288 0.000852	0.0596 0.0312	-3.4 -5.8
1,3-Diolein	1.46419	0.9128	-38.6 to 11 0.0 to 7 -38.6 to -5 25.0 to 50 11.0 to 20 -38.6 to -50 32.0 to 50	I II III liquid I II liquid	0.000292 0.001100 0.000292 0.000861 0.000943 0.000344 0.000812	0.0884 0.0612	25.0 22.7
1-Mono-olein	1.46384	0.9407		I II liquid	0.000943 0.000344 0.000812	0.0600	32.0

^a Temperature interval used to calculate coefficient of expansion and melting dilation was the lowest possible to minimize any effects of premelting.

^b Expansibility and dilation values associated with this form are uncertain because of limitations of the dilatometric technique.

The unit used to express viscosity is denoted a *poise*. If the tangential force per unit area, which one layer of a fluid exerts on an adjacent one, is one dyne when the space rate of variation of the tangential velocity from layer to layer is unity, the viscosity of the fluid is one poise, or 1.00 g. per cm. per second. The 1/100th part of this unit, or the *centipoise* (0.01 poise = 1 centipoise), is quite often used in practice. The absolute viscosity of water at 20.20°C. is 1.00 centipoise, and at 20°C. is 1.005 centipoise. Reference is also often made to *kinematic viscosity*, which is the ratio of the viscosity in poises to the density of a fluid in grams per cubic centimeter.

Various methods have been devised for measuring both *absolute* and *relative* viscosities. The most common of these methods involves the measurement of flow through a tube of very small bore. With colloidal solutions the method of the falling sphere is preferable. Descriptions of the various methods and viscometers used in determining viscosity are given by Reilly and Rae (73). Cannon and Fenske (74) devised a modified viscosity pipette which permits the determination of *kinematic viscosity* with a high degree of precision.

Perhaps the best instrument available for accurately determining the *absolute viscosity* of liquids over a wide range (0.65 to 100,000 centipoises) at temperatures up to 50°C. is the Hoeppler viscometer, which has been adopted by the International Standards Committee on Viscosimetry. Bingham and Jackson (75) have described in detail methods for standardizing viscometers and the preparation of standard reference liquids.

(a) *Viscosities of the Saturated Fatty Acids*

The investigation of the relations between viscosity of liquids and their chemical nature by Thorpe and Rodger (76) is classical in scope and thoroughness. These workers included in their investigation the lower members of the aliphatic series of acids and most of their analogs, including the corresponding anhydrides, alcohols, ethers, monoesters, hydrocarbons, and halides. The viscosities of these compounds were generally determined over their entire liquid range and the data reported in both tabular and graphic form, together with the calculated values for the *molecular viscosity work*, i.e., viscosity times the specific molecular volume of the liquid. Unfortunately, the series of acids was restricted to the first four members as indicated by the data reproduced in Table 119, which gives the coefficients of viscosity in dynes per sq. cm. as a function of temperature in °C. Determinations of the viscosities of the remainder

TABLE 119

Viscosities (dynes/cm.²) of First Four Members of Fatty Acid Series (76)

Temperature, °C.	Formic acid	Acetic acid	Propionic acid	Butyric acid
0	Solid	Solid	0.01519	0.02284
10	0.02245	Solid	0.01286	0.01849
20	0.01782	0.01219	0.01099	0.01538
30	0.01457	0.01036	0.00956	0.01301
40	0.012155	0.00901	0.00841	0.011175
50	0.010315	0.00791	0.00747	0.009715
60	0.00887	0.00700	0.006685	0.008535
70	0.00775	0.00625	0.006015	0.00756
80	0.00682	0.00560	0.005445	0.00674
90	0.00606	0.00505	0.00495	0.006045
100	0.00542	0.004575	0.00452	0.00545
110		0.004165	0.004135	0.00494
120			0.003795	0.004495
130			0.003495	0.00409
140			0.003215	0.00374
150				0.00343
160				0.00314

of the fatty acid series up to and including stearic acid were reported by Dunstan and co-workers (77-79), but the temperature range was relatively narrow, generally from the point of liquefaction to about 95°C. A

TABLE 120

Viscosities of Some Fatty Acids (81)

Acid	Temperature, °F.	Viscosity, centipoises	Acid	Temperature, °F.	Viscosity, centipoises
Lauric	374.0	0.74	Stearic	388.4	1.14
	311.0	1.12		370.4	1.32
	287.6	1.38		334.4	1.70
	266.0	1.67		311.0	2.01
Palmitic	384.8	1.02	Oleic	266.0	3.55
	381.2	1.05		389.3	1.00
	339.8	1.41		384.8	1.02
	332.6	1.62		357.8	1.25
	303.8	1.93		343.4	1.39
	289.4	2.08		324.5	1.50
	285.8	2.14		308.3	1.81
	262.4	2.67		273.2	2.41
				255.2	2.67

similar series of viscosity measurements was reported by Gartenmeister (80) for the acids from acetic to caprylic.

Kern and Van Nostrand (81) determined the viscosities of lauric, palmitic, stearic, and oleic acids in an Ostwald-type viscometer, with the results in Table 120.

TABLE 121
Viscosity of Fatty Acids at 25°C. (82)

Acid	Density, g./cc.	Viscosity, centipoises
Acetic	1.0442	1.126
<i>n</i> -Butyric	0.9535	1.466
<i>n</i> -Valeric	0.9344	1.970
Caproic	0.9238	2.814
Heptanoic	0.9130	3.784
Caprylic	0.9064	5.16

Jones *et al.* (82) determined the variation of viscosity with composition of several fatty acid binary systems with benzene and carbon tetrachloride. The viscosities were measured in Ostwald-type viscosimeters

TABLE 122
Viscosities of Saturated Fatty Acids at Several Selected Temperatures^a

Acid	Temperature, °C.	Viscosity, centipoises ^b
Formic	20.0	1.782
Acetic	20.0	1.219 (1.234)
Propionic	20.0	1.099 (1.109)
Butyric	20.0	1.538 (1.599)
Valeric	20.0	2.30 (2.23)
Caproic	20.0	3.23 (3.19)
Heptanoic	20.0	4.33 (4.35)
Caprylic	20.0 (50.0)	5.74 (2.62)
Nonanoic	20.0 (50.0)	8.08 (3.79)
Capric	50.0 (70.0)	4.34 (2.88)
Undecanoic	50.0	7.30
Lauric	50.0 (70.0)	7.3 (4.43)
Myristic	70.0	5.83 (6.76)
Palmitic	70.0	7.8
Stearic	70.0	9.87 (9.4)

^a Water at 20.20° C. = 1.000 centipoises.

^b Where two values are reported for only one temperature, both appear equally creditable.

in a thermostat maintained at $25.00^{\circ}\text{C.} \pm 0.01^{\circ}$. At compositions corresponding to 100% pure acids, the values obtained are as given in Table 121.

Owing to the differences in freezing points it is not possible to compare the viscosities of an extended series of fatty acids at temperatures below 70° . Comparisons at several selected temperatures are made in Table 122 and graphically over an extended temperature range in Figure 38.

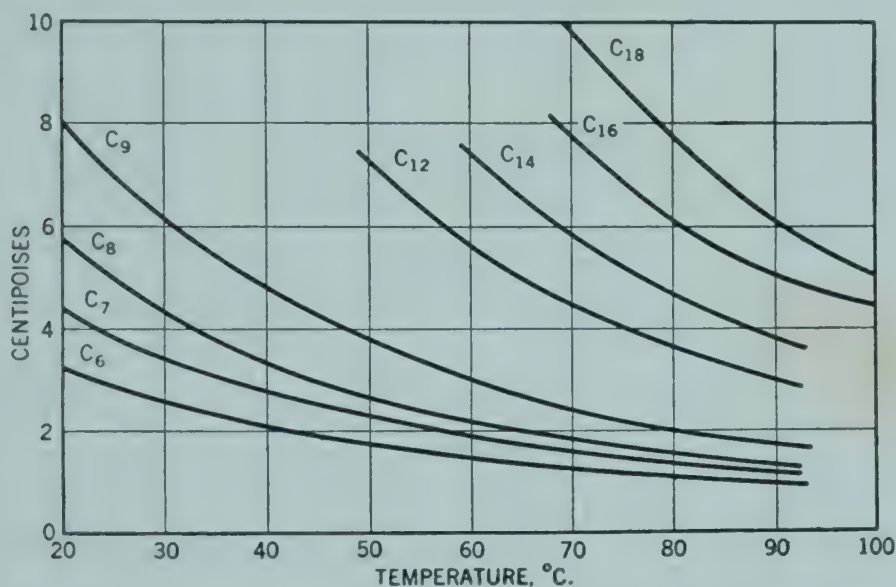


Fig. 38. Temperature-viscosity relationships for the saturated fatty acids from C_6 to C_{18} .

Comparison of the data in Table 119 for acetic, propionic, and butyric acids would indicate that viscosity was an alternating property of the fatty acids, but no alternation is evident in the temperature-viscosity curves of Figure 38 for the acids from C_6 to C_9 .

From Figure 38 it is seen that the viscosity decreases with increased temperature but the change is not linear. However, it has been shown by Dunstan, Hilditch, and Thole (77) and later confirmed by Dunstan *et al.* (78) and by Dunstan (79) that the curves connecting the *logarithms* of the viscosities with molecular weights are approximately linear for the normal fatty acids and the methyl, ethyl, and certain other alkyl esters. This linearity does not appear to hold for the first two acids (formic and acetic) of the series. The curves also depart considerably from strict linearity at the upper end of the series. This departure in the linear relationship may be the result of differences in association of the various

liquids at the particular temperatures at which their viscosities were measured.

Dunstan (79) observed that the series of fatty acids presented several marked peculiarities. The viscosities of formic and acetic acids are much higher relatively than those of the succeeding members, formic acid being more viscous than acetic acid. The average value of the homologous increment throughout the series was found to be considerably in excess of that obtaining in such series as the esters, ethers, paraffins, and ketones, where agreement between the various CH_2 group differences is relatively good.

(b) Viscosities of Alkyl Esters of Saturated Acids

Data with reference to the viscosities of the methyl and ethyl esters of the saturated fatty acids are considerably less extensive than for the corresponding acids. Except for the first three members (76,80), most of the determinations have been reported for single temperatures, and the series is relatively incomplete, as is evident by reference to Table 123. Dunstan et al. (78) determined the viscosities of a number of the fatty acid esters of the higher alcohols, and later Gill and Dexter (83) prepared the methyl, ethyl, propyl, butyl, and amyl esters of the acids from acetic to caproic and determined their viscosities at 25°C . The latter authors plotted the logarithms of the viscosities in poises against the number of carbon atoms in the ester and found the points were scattered about a straight line, but it is difficult to conclude anything of significance from the plot of these data.

TABLE 123
Viscosity of Methyl and Ethyl Esters of Saturated Fatty Acids

Acid	Methyl ester		Ethyl ester	
	Temp., $^\circ\text{C}$.	Viscosity, centipoises	Temp., $^\circ\text{C}$.	Viscosity, centipoises
Formic	20	0.367	20	0.413
Acetic	20	0.383	20	0.452
Propionic	20	0.461	20	0.536
Butyric	20.38	0.572	20	0.666
Valeric	20	0.711	20	0.836
Heptanoic			25	1.11
Caprylic	25	1.26	25	1.38
Nonanoic			25	1.69
Lauric	25	3.08	25	3.08
Palmitic			25	5.76
Stearic			50	3.75

Gros and Feuge (45) determined the viscosities of an extended series of (C_2 to C_{18}) saturated fatty acids and their methyl and ethyl esters at a single temperature ($75^\circ\text{C}.$) with the results given in Table 124.

TABLE 124

Viscosities of Saturated Fatty Acids and Their Esters at $75^\circ\text{C}.$ (45)

Carbon atoms in fatty acid chain	Viscosity, centipoises		
	Acid	Methyl ester	Ethyl ester
2	0.622		0.269
4	0.728	0.328	0.363
6	1.279	0.407	0.537
8	1.855		0.716
10	2.563	0.985	0.999
12	3.836	1.131	1.230
14	5.060	1.528	1.643
16	7.082		2.003
18	9.040	2.360	2.590

The absolute viscosities were calculated for the ethyl esters of the saturated acids from C_6 to C_{18} and the alkyl acetates from hexyl to octadecyl, using data obtained with modified Ostwald viscosimeters by Shigley and co-workers (29). These values are listed in Table 125.

TABLE 125

Absolute Viscosities in Centipoises at Several Temperatures of
Two Series of Alkyl Esters (29)

Ester	$35^\circ\text{C}.$	$50^\circ\text{C}.$	$65^\circ\text{C}.$	$80^\circ\text{C}.$	$95^\circ\text{C}.$
Ethyl caproate	0.8182	0.6734	0.5665	0.4832	0.4174
Ethyl caprylate	1.212	0.9780	0.7954	0.6691	0.5867
Ethyl caprate	1.739	1.353	1.087	0.8974	0.7490
Ethyl laurate	2.444	1.854	1.463	1.177	0.9677
Ethyl myristate	3.318	2.433	1.869	1.489	1.231
Ethyl palmitate	4.459	3.208	2.415	1.892	1.516
Ethyl stearate	5.689	4.041	2.986	2.292	1.831
Hexyl ethanoate	0.9102	0.7390	0.6154	0.5233	0.4491
Octyl ethanoate	1.377	1.084	0.8767	0.7275	0.6137
Decyl ethanoate	2.059	1.574	1.239	0.9963	0.8147
Dodecyl ethanoate	2.820	2.080	1.608	1.285	1.047
Tetradecyl ethanoate	3.850	2.792	2.100	1.639	1.326
Hexadecyl ethanoate	5.114	3.581	2.652	2.053	1.634
Octadecyl ethanoate	6.680	4.542	3.301	2.513	1.976

It has been observed that, in general, a decrease in viscosity of the saturated fatty acids and esters accompanies an increase in temperature, and that this decrease becomes continuously smaller, the higher the temperature. The influence of temperature is greatest in those substances having the greatest viscosity.

(c) *Viscosities of Unsaturated Acids and Esters*

Data relative to the viscosity behavior of the unsaturated aliphatic acids and esters are almost nonexistent. Oleic acid and its geometrical isomer, elaidic acid, are the only long chain unsaturated acids which have received any appreciable attention. Such data as are available are due almost entirely to Thole (84) and to Keffler and McLean (49).

Thole's work on the unsaturated acids and esters was confined to the determination of the viscosities of oleic and elaidic acids, and the corresponding ethyl esters, in amyl acetate solution and at only one temperature, namely, 24.70°C. Keffler and McLean (49) determined the viscosity of relatively pure oleic acid over the temperature range 20° to 90°C., using a specially designed quartz viscometer of the capillary-flow type. These authors also prepared a series of *n*-alkyl oleates and determined the viscosities at 30, 60, and 90°C. The values for the density, viscosity, and fluidity for oleic acid and its esters obtained by Keffler and McLean are reproduced in Tables 126 and 127.

The logarithms of the viscosities of the alkyl oleates were plotted by Keffler and McLean against the number of carbon atoms in the chain but, unlike the normal saturated acid esters investigated by Thole (84), no simple linear relationship was noted. The fluidities of the esters of

TABLE 126
Viscosity of Oleic Acid (49)

Temp., ° C.	Flow time, sec.	Density, d_4^t	Viscosity, poises	Fluidity, rhes
20	1313	0.8906	0.3880	2.96
25	1078	0.8870	0.2764	3.62
30	901	0.8836	0.2301	4.35
35	765	0.8802 ^a	0.1946	5.14
45	558	0.8735 ^a	0.1408	7.10
60	377	0.8634	0.0941	10.63
90	199	0.8429	0.0485	20.63

^a Interpolated.

TABLE 127
Viscosities of *n*-Alkyl Oleates (49)

Ester	Iodine value	Temp., ° C.	Flow time, sec.	Density, d_4^t	Viscosity, poises	Fluidity, rhes
Methyl	85.2	30	149.9	0.8666	0.0488	20.5
		60	107.1	0.8450 ^a	0.0262	38.2
		90	68.8	0.8234 ^a	0.0164	61.1
Ethyl	81.7	30	208.0	0.8622	0.0518	19.3
		60	113.7	0.8409	0.0276	36.2
		90	72.2	0.8192	0.0171	58.5
Propyl	77.9	30	235.8	0.8601	0.0586	17.1
		60	126.3	0.8389	0.0306	32.7
		90	79.0	0.8175	0.0187	53.6
Butyl	74.4	30	261.1	0.8599	0.0649	15.4
		60	137.8	0.8390	0.0334	29.9
		90	87.5	0.8178	0.0207	48.4

^a Interpolated.

oleic acid were observed to be about four times as great as that of the acid, which fact the authors attributed to the very high molecular association of oleic acid. The fluidity of the esters increased about threefold over the temperature range 30 to 90°C., compared to a fivefold increase for the acid. The fluidity of the esters appeared to decrease with increasing molecular weight although the increment per CH₂ group varies from one pair to another.

Treibs (85) determined the viscosities of the methyl esters of the industrially important unsaturated fatty acids at a temperature of 14°C. with the results given in Table 128.

TABLE 128
Viscosities at 14°C. of Methyl Esters of Unsaturated Fatty Acids (85)

Ester	Viscosity, H ₂ O = 1
Oleate	10.2
Linoleate	6.9
Linolenate	5.0
Ricinoleate	13.5
β -Eleostearate	15.8
α -Eleostearate	20.3

Effect of Pressure on the Viscosity of Oleic Acid. The effect of pressure on the viscosity of many liquids was determined by Bridgman (86),

who included oleic acid among the liquids investigated. The oleic acid used in this work was obtained from a chemical supply house and was used without further purification. The viscosity was measured at several pressures and at two temperatures, namely, 30 and 75°C. The results, expressed as logarithms of the relative viscosities as functions of pressure and temperature, and with the viscosity at 30°C. and atmospheric pressure as unity, are given in Table 129. Bridgman used the logarithm of the viscosity instead of the viscosity itself because the variation with pressure was very rapid, and the curve of viscosity against pressure exhibited rapidly varying curvature, whereas the curve of the logarithm of

TABLE 129
Effect of Pressure on Viscosity of Oleic Acid (86,87)

Pressure, kg./sq. cm.	$\log_{10} \eta/\eta^{30}$		η^{30}/η^{75}
	30°C.	75°C.	
1	0.000	9.419	3.811
500	0.306	9.671	4.315
1000	0.616	9.989	4.236
2000		0.255	
4000		0.843	

viscosity against pressure was found to approach a straight line at high pressures and was not too much curved at low pressures. Like practically all liquids, except water, the viscosity of oleic acid increases linearly with pressure, but beyond a pressure of the order of 1000 kg. the rate of increase rapidly increases. Under the influence of increasing pressure, oleic acid solidifies at 30°C. between 100 and 1600 kg. per sq. cm., and at 75°C. it melts below 5000 kg. per sq. cm.

(d) *Specific Viscosity*

Staudinger (87) introduced the term *specific viscosity*, $\eta_{sp.}$, which he defined as the increase in viscosity produced in a solvent by dissolving a unit quantity of a substance in a unit volume of solvent. He related the specific viscosity to the carbon chain length by the expression $\eta_{sp.}/c = KL$, where c is the concentration of a primary molal solution (1.4% = $\text{CH}_2/1000$), K a constant, and L the length in angstrom units of the carbon chain of the compound.

For example, in the case of normal organic compounds such as the aliphatic acids and esters, the specific viscosity of a molal solution may be

expressed as $\eta_{sp.}(1.4\%) = ny + x$, where n is the number of carbon atoms in the chain, y the viscosity of a single carbon atom, and x that of oxygen. For many compounds y is approximately constant. The linearity of the specific viscosity as a function of carbon chain length of the fatty acids and other homologous aliphatic series is evident from Figure 39, which is reproduced from Staudinger's work (87). From the plot of the

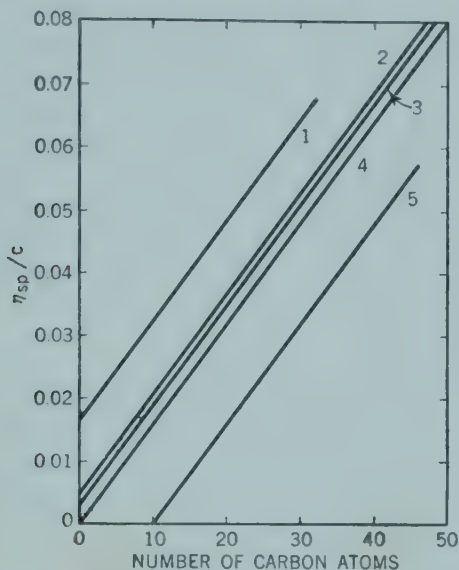


Fig. 39. Relation between specific viscosity (in 1.4% solutions of carbon tetrachloride) to carbon chain length (87) of (1) *n*-fatty acids in pyridine; (2) *n*-fatty acids, (3) esters of *n*-fatty acids; (4) *n*-paraffins; (5) *n*-alcohols.

specific viscosity against the carbon chain length of the various homologous series shown in Figure 39, the values of x for each series can be determined from intercepts on the $\eta_{sp.}/c$ axis.

6. Surface and Interfacial Tension

Between particles of a liquid, as in solids, there are attractive forces which keep the liquid together, and these forces must be overcome by external forces if the particles are to be separated. These forces are molecular in nature and are exerted over only very short distances. The evaporation of a liquid entails overcoming these molecularly attractive forces and the heat required for evaporation is a measure of the strength of the force.

To demonstrate directly the existence of the molecular attractive force of a liquid is very difficult, but the order of magnitude of these forces

can be observed by a simple experiment. If a glass tube is completely filled with water at an elevated temperature and the tube then sealed, it will be found on cooling that the water will continue to fill the tube even after it is cooled to a low temperature. The water will not contract until it has exerted a tensile force of about 73 lb. per sq. in. on the walls of the tube.

These molecular forces within the body of a liquid produce certain remarkable effects at the surface of the liquid. For example, the surface of a liquid tends to contract to the smallest admissible area. The ultimate contraction results in the production of a sphere, because a sphere presents the least surface area for a given volume. The tendency to assume a spherical surface is observed in the formation of raindrops, liquid lead falling from a shot tower, the rounding of a rod of glass or sealing wax when heated, soap bubbles, etc., and this tendency to form a surface of minimum area is a manifestation of the phenomenon of *surface tension*.

Many analogies have been used to illustrate the phenomenon of surface tension. One of the simplest is the consideration of a particle, *A*, in the body of the liquid at some distance below the surface. This particle may be considered as being in the center of a sphere of force produced by the attractive force of all the surrounding particles. If a second particle, *B*, is situated at or very close to the surface, it too is subject to a sphere of force which is, however, not uniform since the particle is more strongly attracted by the force due to surrounding liquid than it is to the vapor above it. It will, therefore, be attracted inward more than outward. To take a particle from position *A* to position *B* requires that work be done against this inward attraction.

When the surface of a liquid is increased, for example, in stretching a soap film, more particles are drawn to the surface; hence work is done by the stretching force and an opposing force is overcome. The required stretching force is parallel to the surface and the liquid exerts an opposing or contractile force parallel to the plane of the surface and this force is known as *surface tension*. Although the field of force giving rise to surface tension is actually downward, it is defined and expressed mathematically as a *force parallel to the surface*. Thus, surface tension is defined as the force in dynes per unit length (1 cm.) of surface of liquid in a direction parallel to the surface.

The tension produced at the surface of a liquid in contact only with vapors of the liquid phase, or with air, or an inert gas such as nitrogen, is referred to as *surface tension*, whereas the tension at the interfacial sur-

face of a solid-liquid system or a liquid-liquid system is referred to as *interfacial tension*. Strictly speaking, surface tension should refer only to a liquid-vapor interface containing only one component.

The surface tension and the interfacial tension of liquids have become of importance in the control and development of industrial processes. By means of surface tension measurements small changes in the concentration of impurities may be detected during the refining of petroleum. The effect of oxidation on lubricating oils is readily detected by changes in the surface tension. Likewise, the presence of very small amounts of alkali soaps remaining in vegetable oils after refining may be detected by surface tension measurements. This property is also of importance in the application of vegetable oils in the tinning of sheet steel to produce tin plate and in other industrial operations involving emulsification, miscibility, solubility, and absorption phenomena.

(a) Measurement of Surface Tension

There are a number of methods available for measuring surface tension, all of which can be classified into two groups, namely, static or dynamic methods. The static methods include (a) direct measurement of curvature of the liquid surface; (b) flat drops and bubbles on surfaces; (c) capillary rise; (d) adhesion plates and rings; (e) determination of drop weights or volume; (f) gas-bubble pressure; and (g) sessile bubble method. Included in the dynamic methods are (a) oscillating jets; (b) vibrating jets; (c) measurement of ripple waves; and (d) centrifugal. Many modifications of these methods, as well as other methods of minor importance, have been proposed.

The three most common methods generally used in measuring the surface tension of liquids are (1) the capillary height or rise, (2) the drop weight, and (3) the method of maximum pull on a ring. These methods are described in standard textbooks and manuals on physical chemistry. Of the three methods the drop-weight method probably is the most precise, since it gives results accurate to 0.1% at a water interface and about 1.0% at a mercury interface.

The capillary-rise method, which observes the behavior of a liquid in a capillary tube, has the simplest mathematical derivation, and assumes that the liquid wets the capillary tube perfectly, and therefore at a contact angle of zero. Sugden (88) made a careful study of this method, and concluded that accurate calibration of tube size and table of corrections were required.

The drop-weight or volume methods are based upon determining the weight or volume of drops falling from a vertical tube of known size. Considerable care is needed to use this method, which was investigated thoroughly by Harkins and Brown (89).

The ring method measures the force required to pull a wire ring out of the liquid surface. It is the simplest and most rapid method of measuring surface tension.

Hauser and co-workers (90) conducted a comparative investigation of the drop-weight and ring methods by means of a high-speed camera. Stroboscopic analyses of these two methods led these investigators to suggest that neither is ideal from the standpoint of accuracy. They concluded that the capillary-rise method gives the most accurate results.

Although possibly somewhat less accurate, the method of maximum pull on a ring is most commonly used and is especially applicable to the measurement of the surface tension of fats and oils and their derived products. The application by du Noüy (91) of the torsion balance to the ring method of determining surface and interfacial tension has simplified the method and increased the rapidity with which measurements can be made. With the best du Noüy instrument, surface tension measurements of fats and oils can be made with a precision in good agreement with those obtained by the capillary-rise method and with a reproducibility of the order of 0.05 dyne. Both upward and downward interfacial measurements, as well as surface tensions, can be made with the same instrument.

The du Noüy tensiometer, illustrated in Figure 40, consists of a sensitive torsion balance which applies a slowly increasing force to an accurately constructed platinum-iridium ring in contact with the surface of the liquid under measurement. The amount of applied force is indicated upon a circular graduated scale which, when calibrated, gives readings in dynes of force. A rough approximation of the surface tension by the du Noüy method can be made as follows (91): The force necessary to break the ring away from the surface is equal to the surface tension of the liquid multiplied by twice the length of the loop, or,

$$\gamma = P/4\pi r$$

where P is the breaking force on the ring in dynes and r is the radius of the ring in cm. For a detailed discussion of the application of the du Noüy ring method of determining surface and interfacial tensions of liquids, as well as the comparative accuracy of the method, the reader is

referred to Adam's *The Physics and Chemistry of Surfaces* (92), as well as to the work of Alexander and Teorell (93), Zuidema and Waters (94), and others.

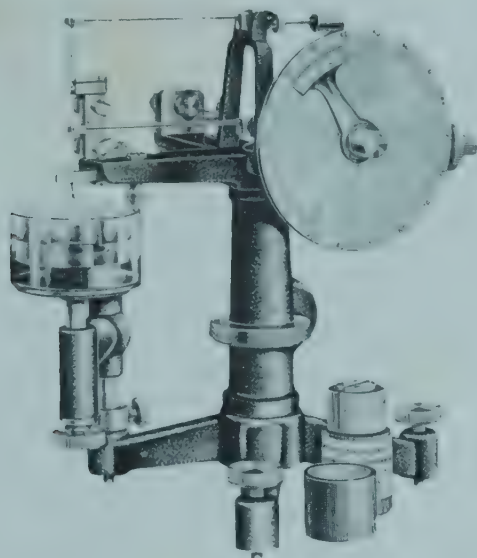


Fig. 40. Du Noüy tensiometer (Courtesy Central Scientific Company).

(b) Surface Tension of Fatty Acids and Esters

Despite the availability of equipment, the simplicity of the method, and the value and utility of surface and interfacial tension data, relatively few systematic measurements were reported prior to 1945 for these important properties of the fatty acids and esters until recently.

The surface tension of the fatty acids varies with temperature, decreasing with increasing temperatures and reaching zero at the critical temperature. For the greater part of the temperature range, the relation between surface tension and temperature is nearly linear. The interfacial tension at the phase boundary is generally influenced more by the presence of impurities than is the case with surface tension.

In 1929, Hunten and Maass (95) reported the results of a systematic investigation of the surface tension of the series of saturated *n*-fatty acids from propionic to stearic. Measurements were made by the capillary-rise method, from the approximate melting points of the acids to about 150°C. The values for surface tension, calculated at selected temperatures from the data of Hunten and Maass, are given in Table 130.

TABLE 130
Surface Tension (dynes/cm.) of *n*-Fatty Acids at Selected Temperatures (95)

Temp., °C.	C ₃	C ₄	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₇	C ₁₈
-35	32.8									
-20	31.0		31.2							
-10	29.9		30.7							
0	28.8		29.7							
10	27.5	27.7	28.5							
20	26.3	26.9	27.5	28.3	28.2					
30	25.3	25.9	26.6	27.7	27.8					
40	24.4	25.0	25.8	26.6	27.3					
50	23.6	23.8	25.1	25.8	26.9	28.1				
60	21.7	22.8	24.2	24.6	26.3	27.3	28.4			
70	20.7	21.8	23.4	23.7	25.2	26.6	27.4	28.2	27.6	28.9
80	19.8	20.8	22.5	22.8	24.7	25.8	26.6	27.5	27.0	28.6
90	19.1		21.6	22.0	23.4	24.8	25.6	26.7	26.0	27.5
100	18.7			21.6	22.7	24.1	24.9	26.1	25.3	26.7
120	16.5				21.1	22.5	23.5	24.5	24.1	25.1
140	14.9					20.9	22.0	22.9	22.5	23.8

In 1952, Gros and Feuge (45) reported the results of a systematic investigation of the surface and interfacial tensions of the homologous series of saturated even-numbered *n*-fatty acids from acetic to stearic, and their methyl and ethyl esters. The numerical values obtained for these properties are given in Table 131. The values of the surface ten-

TABLE 131
Surface and Interfacial Tensions of Saturated *n*-Fatty Acids
and Their Methyl and Ethyl Esters at 75°C. (45)

Carbon atoms in fatty acid chain	Surface tension, dynes/cm.			Interfacial tension against water, dynes/cm.		
	Fatty acid	Methyl ester	Ethyl ester	Fatty acid	Methyl ester	Ethyl ester
2	19.6		17.8			
4	21.6		19.0			
6	23.0	21.0	20.8	2.1	13.9	14.6
8	24.2	22.1	21.9	5.8	17.2	18.2
10	25.1	23.3	23.1	8.0	20.0	21.2
12	25.9	24.3	23.9	8.7	22.0	22.9
14	26.8	25.0	24.9	9.2	23.5	24.3
16	27.3	25.7	25.7	9.2	25.5	25.5
18	27.7	26.1	26.1	9.5	26.2	25.2

sions of the fatty acids were found to be consistently about 2 dynes/cm. higher than the corresponding values for the ethyl esters, and about 1.8 dynes/cm. higher than for the methyl esters. The interfacial tension of the acids is lower than for the esters.

The sucrose monoesters of a number of the higher molecular weight fatty acids were prepared by Osipow *et al.* (96) and their surface and interfacial tensions were measured with the du Noüy tensiometer, with the results given in Table 132.

TABLE 132
Physical Properties of Sucrose Esters (96)

Ester	Softening point, °C.	Surface tension, dynes/cm. ^a				Interfacial tension, dynes/cm. ^{a,b}			
		Concentration, %							
		1.0	0.2	0.1	0.05	1.0	0.2	0.1	0.05
Laurate	90-91	33.4	33.4	33.7	35.6	7.6	7.1	7.9	8.4
Myristate	67-69	33.1	33.1	34.8	34.8	7.3	6.3	7.0	7.4
Palmitate	60-62	33.7	33.7	33.7	35.0	6.3	5.9	6.2	6.2
Oleate	50-54	31.8	30.8	31.5	32.7	5.4	5.0	5.0	6.2
Stearate	52-53	33.5	33.1	34.0	33.7	6.2	6.6	7.7	7.2

^a Aqueous solutions at room temperature.

^b Against Nujol.

Vogel (36) prepared the alkyl esters of the first five members of the homologous aliphatic *n*-alcohols and most of the normal saturated acids from C₁ to C₁₂ and of the first three symmetrical dibasic acids. These preparations were carefully purified and their surface tensions determined at 40°C., with the results given in Table 133.

Surface-tension measurements of aqueous solutions of some pure amine salts of palmitic acid were made by Mod *et al.* (96a). These salts were about equal in ability to lower aqueous surface tension; but the *n*-amylamine and isoamylamine salts were vastly superior in ability to lower the water-Nujol interfacial tension. A concentration of 0.5% of either of these two salts was sufficient to reduce the interfacial tension below 1 dyne/cm. The surface properties of the amine salts of palmitic acid are given in Table 133a.

In the course of an investigation of the adhesion of paint coatings to steel plate, Miller (97) prepared a series of pure esters of the commercially important unsaturated fatty acids and determined several of

TABLE 133
Surface Tension at 40°C. (dynes/cm.) of Alkyl Esters of
Carboxylic and Dicarboxylic Acids (36)

Ester	Methyl	Ethyl	<i>n</i> -Propyl	<i>n</i> -Butyl	<i>n</i> -Amyl
Formate		21.0	22.0	22.9	23.8
Acetate	22.6	21.1	22.1	23.3	23.4
Propionate	22.4	21.9	22.5	23.2	
<i>n</i> -Butyrate	22.9	22.3	22.9	23.7	24.2
Isobutyrate	21.4	20.9	21.6	22.3	
<i>n</i> -Valerate	23.6	23.0	23.6	24.1	24.3
Isovalerate	22.1	21.5	22.5	23.2	
Caproate	24.2	23.8			
Heptanoate	24.9	24.5			
Caprylate	25.7	25.8			
Caprate	26.6	26.3	26.5	26.7	
Laurate	26.8	26.5	27.3	27.3	
Oxalate ^a		29.7	28.2	27.8	27.9
Succinate ^a	33.8	29.7	28.8	28.8	28.8
Adipate ^a	33.5	30.2	29.8	29.6	29.6

^a Diesters of the dicarboxylic acids.

TABLE 133a
Surface and Interfacial Tensions at 27°C. (dynes/cm.) of Aqueous
Solutions of Some Amine Salts of Palmitic Acid^{a,b} (96a)

Palmitic acid salt of	Concentration in wt. %				
	0.5	0.2	0.1	0.05	0.01
<i>n</i> -Amylamine	34.9, <i>0.6</i>	34.4, <i>0.8</i>	33.8, <i>0.6</i>	32.9, <i>0.6</i>	40.4, <i>10.9</i>
Isoamylamine	34.3, <i>0.6</i>	34.8, <i>0.5</i>	33.7, <i>0.6</i>	33.2, <i>0.6</i>	42.3, <i>4.8</i>
2-Amino-2-methyl-1-propanol	36.8, <i>3.2</i>	35.1, <i>8.2</i>	35.1, <i>8.3</i>	32.5, <i>13.8</i>	43.0, <i>32.8</i>
2-Amino-2-ethyl-1,3- x propanediol	35.4, <i>6.4</i>		32.7, <i>20.2</i>		48.5, <i>37.2</i>
2-Amino-1-butanol	35.3, <i>2.2</i>	33.8, <i>6.8</i>	33.4, <i>7.7</i>	37.9, <i>12.2</i>	44.0, <i>32.5</i>
Cyclohexylamine ^c			59.9, <i>37.2</i>		
1-Cyclohexylamino-2-propanol			35.8, <i>29.8</i>		
Morpholine	28.1, <i>13.9</i>				43.9, <i>16.6</i>

^a Values in italics represent interfacial tensions at Nujol surface.

^b The surface tensions of water and Nujol and the interfacial tension at water-Nujol interface were 72.7, 38.5, and 53.1 dynes/cm., respectively.

^c Salt of capric acid.

their surface characteristics. The surface and interfacial tensions of these esters were determined by the drop-profile method of Andreas *et al.* (98), with the results given in Table 134, together with the densities for the corresponding temperature. The interfacial tension of methyl linoleate was slightly increased by the addition of 1.78% of free linoleic acid.

TABLE 134
Surface and Interfacial Tensions Against Water of
Unsaturated Fatty Acids at 25°C. (97)

Ester	Density, 25°/3.98°C., g./ml.	Surface tension, dynes/cm.	Interfacial tension, dynes/cm.
Methyl oleate	0.8703	31.2	24.6
Methyl linoleate	0.8824	31.8	24.3
Methyl linolenate	0.8961	32.6	23.9
Methyl β -eleostearate	0.8985	32.5	24.9
Glycol dilinoleate	0.9030	32.1	9.8
Glyceryl trilinoleate	0.9169	32.6	6.8

Some miscellaneous data for the surface and interfacial tensions of various fatty acids and esters at one or more temperatures have been published (99–101), but it is difficult to determine the reliability of these isolated determinations; hence they are omitted here.

(c) Surface Tension of Glycerides

More than forty years ago (1917), Jaeger (102) published the results of a comprehensive investigation of the surface tension of triglycerides. His values for the surface tension of glycerides against water and benzene agree with the values accepted today. Some of these values are presented in Table 135.

Joglekar and Watson (103) determined the surface tension of some triglycerides by the maximum bubble pressure method at several temperatures. At the temperature at which all can be compared, 80°C., the values given for tricaprin, trilaurin, trimyristin, tripalmitin, and tristearin are 25.9, 26.6, 27.2, 27.6, and 28.1, respectively.

Benerito *et al.* (104) reported data for the surface tension at five temperatures, and the interfacial tensions against water at two temperatures for sixteen pure synthetic glycerides. The method of measurement used was that described by Nevin *et al.* (105). The results, which show the

TABLE 135
Surface Tension (dynes) of Some Triglycerides (102)

Triglyceride	0°C.	50°C.	100°C.	150°C.
Triformin			39.0	33.9
Triacetin	35.1	34.0	30.1	25.0
Tributylin	31.8	29.0	25.6	22.0
Tricaproin	31.6	28.2	25.5	22.7
Tricaprylin	30.1	27.8	25.3	22.8
Tricaprin		27.2	24.6	21.5
Trilaurin			27.2	24.7
Tripalmitan			28.0	25.2
Tristearin			27.7	23.9
Triolein	37.4	32.6	29.4	27.2

effects of degrees of unsaturation, esterification, and *cis-trans*-isomerism on these surface phenomena, are given in Table 136.

TABLE 136
Surface Phenomena of Glycerides at Various Temperatures (104)

Compound	Surface tensions, dyne/cm.					Interfacial tensions against water, dyne cm. ⁻¹	
	20°C.	40°C.	60°C.	80°C.	100°C.	25°C.	75°C.
Triacetin	35.15	33.12	31.09	29.06	27.03	3.33	
Tributylin	27.98	26.39	24.80	23.21	21.57	11.90	
Tricaproin	26.32	25.16	24.00	22.84	21.68	18.56	17.32
Tricaprylin	25.68	24.44	23.19	21.95	20.68	14.60	14.16
Tripalmitin ^a	(27.69)	(26.41)	(25.13)	23.85	22.57		11.01
Tristearin	(29.61)	(28.26)	(26.90)	25.54	24.18		10.43
Triolein	28.71	27.34	25.95	24.56	23.17	14.61	(13.47) ^b
Trielaidin	(25.78)	(24.38)	22.98	21.58	20.18		11.56
Trilinolein	20.28	19.70	19.13	18.56	17.99	13.16	
1,2-Diaceto-3-olein	21.88	20.82	19.75	18.69	17.62	7.46	
1,2-Diaceto-3-stearin	(30.13)	(28.27)	26.40	24.53	22.66		2.90
1-Monostearin	(23.35)	(22.17)	(21.00)	(19.82)	18.64		
1-Monopalmitin	(26.16)	(24.79)	(23.45)	22.12	20.78		
1,3-Dipalmitin	(24.93)	(24.00)	(23.07)	22.15	21.23		
1,3-Dioleo-2-palmitin	26.49	25.60	24.72	23.83	22.94	14.50	12.26
Tripelargonin	24.25	23.12	21.99	20.86	19.73	20.16	

^a Values enclosed in parentheses are hypothetical for temperatures below the melting point of the glyceride.

^b Value obtained immediately after introduction of water phase.

Fatty acids and their derivatives not only exhibit marked surface and interfacial tensions, but they also exert effects, often very marked, on the interfacial tension of many liquids. For example, Gilbert (106) showed that the surface tensions of liquid petrolatum was changed from 31.2 to 30.4 dyne/cm. at 20°C., with the addition of 0.0197 moles of myristic acid to 1000 g. of hydrocarbon product. Again, as first established by Donnan (107), the solution of a fatty acid in a triglyceride produces a decrease of the interfacial tension of the latter. An excellent review of the effects of fatty acids and derivatives on the surface and interfacial tensions of different liquids is given by Dervichian (108).

(d) Surface Tension of Fatty Acid Soaps

Because of the importance of surface tension phenomena to detergency, various investigations have been made of the surface tension of aqueous soap solutions. Data available up to 1929 with respect to the surface tension of such solutions, which include the soaps of lauric, myristic, palmitic, and stearic acids, and dilute solutions (0.1%) of the acids from C₁₀ to C₂₀ have been assembled by McBain (109).

The surface tension of sodium oleate has been more thoroughly investigated than that of any other soap (91). Cavier (110) measured the surface tension of the sodium soaps of oleic, linoleic, linolenic, ricinoleic, dibromoricinoleic, lauric, α -bromolauric, hydroxystearic, hydnocarpic, and chaulmoogric acids. He concluded from these measurements that the greater the degree of unsaturation in the hydrocarbon chain, the lower was the surface tension. Ricinoleic acid, containing a hydroxyl group and one double bond, was found to give a greater lowering at high concentrations and a lesser lowering of surface tension at low concentrations than was observed with the soaps of the saturated acids.

A very comprehensive study of the surface tension-concentration relationships of soaps in 0.1% sodium carbonate solution has been reported by Breusch and Ulusoy (111). These workers investigated several homologous series containing 10 to 20 carbon atoms, including the aliphatic normal acids, both saturated and unsaturated, branched-chain acids, oxy acids, alkyl esters of branched-chain acids, and other compounds. Typical of the data obtained by Breusch and Ulusoy are those for the surface tensions of the soaps of some saturated acids given in Table 137.

Changes in surface tension of aqueous soap solutions, as functions of concentration and temperature, were reported by Angelescu and Davidescu (111a). Surface tension was found to increase with increasing soap con-

TABLE 137
Surface Tension (dyne/cm.) of Sodium Soaps of Saturated
Fatty Acids at 28°C. (111)

Acid	2%	0.5%	0.2%	0.1%	0.05%	0.02%	0.01%	0.005%	0.001%
Lauric	33.6	32.9	42.6		55.6	64.1		69.5	
Myristic	28.5	28.5	29.9		37.5	49.5		63.0	
Palmitic			25.5	27.0		29.9	34.2		64.9
Stearic						38.6	40.2		66.4

centration. Stearate soaps showed decreases in surface tension greater than did the palmitates, and potassium soaps of these acids had less surface tension than the sodium soaps. As the temperature increased, the surface tension of the sodium soaps increased, while that of the potassium soaps decreased. The surface tensions are recorded in Table 137a.

TABLE 137a
Surface Tension (dyne/cm.) of Pure Soap Solutions (111a)

Soap	Concen- tration ^a	Surface tension, dyne cm. ⁻¹		
		60°C.	50°C.	40°C.
Sodium stearate	0.10	25.1	25.7	
	0.15	27.0	26.6	
	0.20	27.4	27.1	
Potassium stearate	0.10	23.2	26.6	
	0.20	24.2	26.4	
Sodium palmitate	0.10	30.1	29.2	28.2
	0.15	30.1	29.2	28.6
	0.20	31.0	30.2	30.2
Potassium palmitate	0.10	28.4	28.1	
	0.20	28.7	28.7	
Sodium oleate	0.20	26.5	26.4	26.5

^a Normality.

According to Biswas and Mukherji (111b) surface and interfacial tensions of the sodium salts of monoglyceride sulfates of C₁₂ to C₁₈ saturated fatty acids, and of oleic and linoleic acids, decreased with increase in concentration. The myristic and oleic surfactants, representing the saturates and unsaturates, respectively, are reported to have the best tensioactive properties of the materials tested. This activity is explained on the basis of optimum hydrophylic-hydrophobic balance by the myristic and oleic products. The surface properties of this series of materials are given in Table 137b.

TABLE 137b
Surface (γ) and Interfacial (γ_i) Tension (Dynes/cm.)^a at $25 \pm 0.2^\circ\text{C}$. of Solutions of Sodium Salts
of Fatty Acid Monoglyceride Sulfates (111b)

Concen- tration (%)	Fatty acid in the surfactant											
	Lauric		Myristic		Palmitic		Stearic		Oleic		Linoleic	
	γ	γ_i	γ	γ_i	γ	γ_i	γ	γ_i	γ	γ_i	γ	γ_i
0.001	71.0	..	52.2	..	70.6	..	71.9	..	64.2	..	64.3	..
0.002	69.0	..	46.0	..	67.1	..	71.9	..	61.2	..	61.1	..
0.005	56.1	53.8	38.5	51.1	55.3	52.0	59.1	53.8	57.7	53.8	58.2	50.2
0.01	50.5	52.0	37.8	46.8	49.1	47.3	49.2	52.2	55.7	51.8	56.0	46.1
0.02	42.0	48.5	33.6	39.4	47.5	42.6	48.1	46.5	49.5	43.6	49.5	40.0
0.05	36.3	44.7	27.2	29.9	46.1	32.7	46.0	35.3	43.1	32.7	43.2	32.7
0.10	33.9	38.9	26.1	18.8	45.9	21.4	46.0	25.6	36.0	21.7	37.1	25.2

^a Interfacial tensions of the aqueous solutions against *n*-heptane. (Interfacial tension of distilled water against *n*-heptane was 53.8 dynes/cm.).

Much work has been done on the measurement of the surface tension of surface active agents in solution, and the effect of electrolytes, but little on the effect of organic nonelectrolytes. Bose and Mehrotra (111c) concluded that the addition of free hydroxide to soap solutions in the presence of different concentrations of the nonelectrolyte butanol-1 decreased the surface tension of the solutions. As the concentration of alcohol increased from 5% to 50%, the surface tension decreased until a constant value was reached at alcohol concentrations between 30 and 50%. Above an alcohol concentration of 50%, surface tension increased. The surface tension of the system described is given in Table 137c.

7. Refractivity and Refractive Index

It has been known since ancient times that a beam of light is more or less deviated or refracted in passing from air into water, and the law of refraction was established by Willebrod Snell in 1621. He found by experiment that the ratio of the sines of the angles of incidence and of refraction is a constant at the boundary between two media, i.e., $\sin i / \sin r = n$. The refractive index, n , of any substance is the ratio of the velocity of light in a vacuum to the velocity of light in the substance. It is a measure of the interaction of the electrostatic and electromagnetic fields set up by atoms in a molecule with the electromagnetic and electrostatic components of the traversing light waves, and it is dependent upon the intermolecular attractive forces which determine molecular volume and internal pressure.

Except for the thermal-expansion effect, the refractive index is independent of temperature, but it varies with the wavelength of light, therefore it is necessary to specify the wave length at which any given measurement of the refractive index is made. This is usually done by means of a subscript, e.g., n_D indicates the refractive index was observed with the sodium D line; n_{α} the hydrogen α -line, n_{5461} the green line of mercury, etc.

Related to the refractive index are specific refractivity, molecular refraction, and molecular dispersion. The dependence of the refractive index upon specific volume has been related by the equation $r = (n^2 - 1)/d$, where r is the *specific refraction* and d the density. A more useful relation proposed by Lorenz (112) and Lorentz (113) is:

$$r = [(n^2 - 1)/(n^2 + 2)] \cdot 1/d$$

a relation nearly independent of temperature and pressure. The difference between the specific refractions for any two wave lengths is a meas-

TABLE 137c
Surface Tension (dynes/cm.) at $35 \pm 0.05^\circ\text{C}$. in the System: Water—0.2 N Sodium Salts of Fatty Acids—
Butanol-1 in the Presence of Free Acids

Acid Neutral- ized, °C	Sodium salts of the acids	Concentration of butanol-1, volume %									
		5	10	20	30	40	50	60	70	80	90
25	Lauric									23.13	23.46
	Myristic									23.38	23.66
	Palmitic									22.47	23.30
	Stearic									23.54	
50	Lauric		22.77						22.96	23.01	23.09
	Myristic		23.36						23.24	23.35	23.36
	Palmitic								22.04	22.24	22.29
	Stearic								23.30	23.47	
75	Lauric	24.07	23.79	22.15	22.14	22.11	22.11	22.65	22.81	22.89	22.94
	Myristic	24.86	24.76	23.18	22.84	22.76	22.72	22.83	23.17	23.30	gel
	Palmitic	gel	25.71	23.20	22.64	22.47	21.76	21.82	21.96	22.17	gel
	Stearic	gel	24.47	23.54	23.12	22.92	22.82	23.11	23.28	23.38	gel
100	Lauric	25.93	23.83	22.06	22.03	22.01	22.00	22.73	22.80	22.96	23.05
	Myristic	26.90	24.92	23.08	22.77	22.77	22.76	22.81	23.11	23.20	gel
	Palmitic	gel	26.12	23.25	22.97	22.89	21.77	21.78	21.85	21.92	gel
	Stearic	gel	26.40	23.43	22.99	22.89	22.84	23.03	23.98	23.28	gel

ure of the dispersion for these two wave lengths. This difference is called the *coefficient of dispersion* and is expressed as $\Sigma_{\alpha - \beta}$.

The *molecular refraction*, M , of a substance is obtained by multiplying its specific refraction by the molecular weight. The difference between the molecular refractions measured at any two wave lengths is known as the *molecular dispersion* and is designated as $M_{\alpha - \beta}$.

(a) *Refractive Indices and Molar Refractivities of Saturated Acids and Esters*

The refractive index, specific refractivity, and molecular refractivity are especially useful properties of fatty acids, esters, and natural fats. Although numerous isolated measurements have been made of the refractive indices of various fatty acids, esters, glycerides, and natural fats, only a few systematic investigations, and these are of very recent origin, have been made of these substances. Some of the investigations are more than fifty years old (114,115) and were made with products of dubious purity.

The earlier reported determinations of the refractive indices of the fatty acids were made at arbitrary and scattered temperatures, although the work of Falk (116) published in 1909 on butyric acid is an exception to this statement. Falk determined the densities and refractive indices of a sample of butyric acid at 10° intervals from 10 to 80°C.

In 1942, Dorinson *et al.* (44) reported the results of their systematic investigation of the refractive indices of the saturated fatty acids from caproic to stearic. Determinations were made over a temperature range of 20 to 80°C. for the lowest molecular weight acids and from just above the melting point to 80°C. for the remainder of the series. Their results were presented in tabular form, and are reproduced in part in Table 138 and in graphic form in Figure 41.

The values for the refractive indices in Table 138 were not corrected for the effect of temperature on the refractometer prism, whereas those in Figure 41 have been corrected by applying the factor $0.00006 (t - 20)$, where t is the temperature at which the measurement was made. The refractivities for each acid fall on a straight line between 40° and 80°C. but, as indicated by the dotted line, deviate from linearity below 40°C.

These authors calculated the molar refractivities at 80°C. by the Lorenz-Lorentz equation:

$$R_m = [(n^2 - 1)/(n^2 + 2)] \cdot M/d$$

and with the values of n from Table 138 and of d from Table 100.

Table 139. From the results of Dorinson *et al.*, Davis (117) constructed a nomograph for use in determining the refractive index of the normal saturated acids from caproic to stearic at any given temperature within the applicable temperature range.

Few data comparable to those for the fatty acids are available for the refractive indices of the monoesters of these acids. Incidental to an investigation of the degree of separation obtainable by fractional distillation, Wyman and Barkenbus (118) determined the refractive indices of

TABLE 139
Molar Refractivities of Normal Saturated Fatty Acids (44) at 80°C.

Acid	R_m (exptl.) ^a	R_m (calcd.) ^b	Acid	R_m (exptl.) ^a	R_m (calcd.) ^b
Caproic	31.70	31.75	Tridecanoic	64.35	64.33
Heptanoic	36.34	36.40			
Caprylic	41.08	41.06	Myristic	69.00	68.99
Nonanoic	45.66	45.71	Pentadecanoic	73.65	73.64
Capric	50.36	50.37			
Hendecanoic	55.02	55.02	Palmitic	78.30	78.30
Lauric	59.73	59.68	Margaric	83.01	82.95
			Stearic	87.59	87.61

^a Calculated from the Lorenz-Lorentz equation.

^b Calculated from the equation of Dorinson *et al.* (44).

the methyl esters of the even-numbered fatty acids from caprylic to stearic. The measurements, which were made at only one temperature (45°C.) with an Abbe refractometer, are given in Table 140.

TABLE 140
Refractive Indices of Methyl Esters of Even-Numbered
Fatty Acids from Caprylic to Stearic (118)

Methyl ester	n_D^{45}
Caprylate	1.4069
Caprate	1.4161
Laurate	1.4220
Myristate	1.4281
Palmitate	1.4317
Stearate	1.4346

The work of Wyman and Barkenbus was extended by Mattil and Longenecker (119), who determined the variation in refractive index as a func-

tion of temperature for the series of methyl esters from caprate to stearate. They also determined the variation in refractive index as a function of composition of a series of binary mixtures of the methyl esters of both saturated and unsaturated acids. These relationships which are shown in Figures 42 and 43 are especially useful in following the fractionation of fatty acid mixtures by distillation or by low-temperature crystallization.

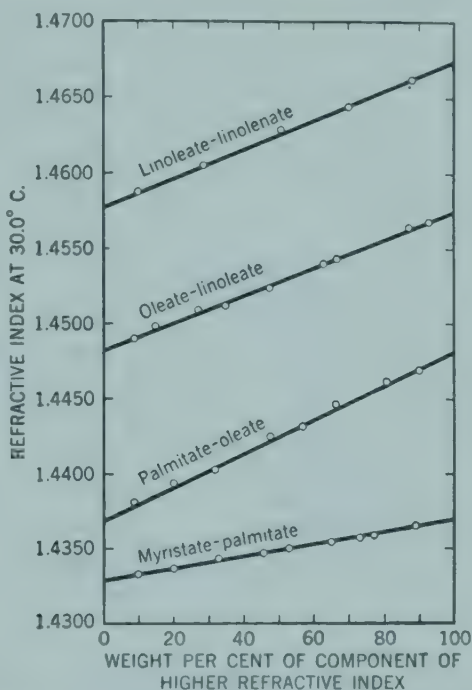
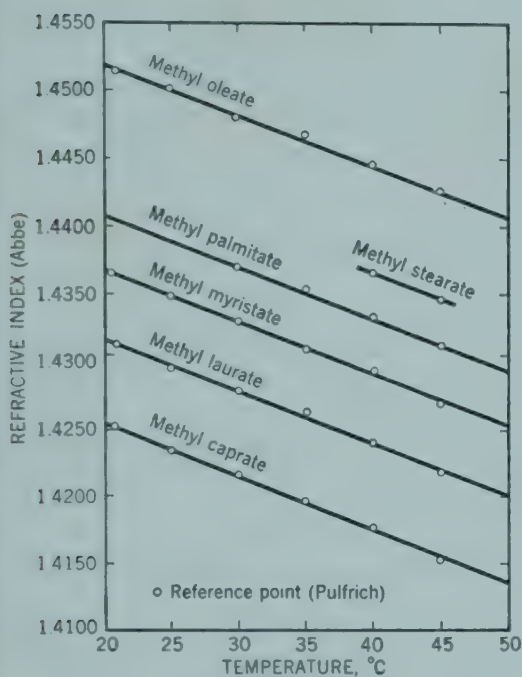


Fig. 42. Relation of refractive index to temperature for highly purified methyl esters (119).

Fig. 43. Relation of refractive index to weight-percentage composition of binary mixtures of highly purified methyl esters (119).

Craig (120) determined the refractive indices of several high molecular weight acids and their methyl esters, and developed equations for calculation of refractive indices at any temperature. The experimental results and equations developed therefrom are given in Table 141.

Using a calibrated Valentine precision refractometer with prism temperature controlled to $\pm 0.05^\circ\text{C}$., Shigley *et al.* (29) determined the refractive indices of the ethyl esters of a series of saturated aliphatic acids from C_6 to C_{18} and a series of alkyl acetates from hexyl to octadecyl, with the results given in Table 142.

TABLE 141
Refractive Indices and Equations for Some Fatty Acids and
Their Methyl Esters (120)

Material	Refractive index, experimental	Equation, R.I.t. ^a
	n_D^{35}	
Methyl oleate	1.44656	1.45968-0.000377t
Methyl eicosenoate	1.44833	1.46134-0.000372t
Methyl erucate	1.44977	1.46288-0.000369t
Oleic acid	1.45442	1.46677-0.000354t
Eicosenoic acid	1.45574	1.46805-0.000351t
Erucic acid	1.45674	1.46892-0.000346t
	$n_D^{60.2}$	
Methyl palmitate	1.42549	1.44830-0.000379t
Methyl stearate	1.42897	1.45149-0.000375t
Methyl arachidate	1.43165	1.45363-0.000366t
Methyl behenate	1.43391	1.45554-0.000358t
	$n_D^{85.6}$	
Palmitic acid	1.42545	1.45589-0.000355t
Stearic acid	1.42830	
Arachidic acid	1.43066	
Behenic acid	1.43257	

^a R.I.t. = Refractive index at temperature *t* °C.

TABLE 142
Refractive Indices^a of Two Series of Alkyl Esters at Various Temperatures (29)

Substance	20°C.	25°C.	30°C.	35°C.	40°C.
Ethyl caproate	1.4072	1.4050	1.4029	1.4007	1.3985
Ethyl caprylate	1.4178	1.4157	1.4136	1.4116	1.4095
Ethyl caprate	1.4254	1.4235	1.4215	1.4195	1.4173
Ethyl laurate	1.4315	1.4295	1.4275	1.4255	1.4235
Ethyl myristate	1.4361	1.4340	1.4321	1.4302	1.4282
Ethyl palmitate			1.4363	1.4343	1.4324
Ethyl stearate				1.4375	1.4355
Hexyl ethanoate	1.4091	1.4068	1.4046	1.4023	1.4002
Octyl ethanoate	1.4193	1.4171	1.4150	1.4128	1.4108
Decyl ethanoate	1.4268	1.4247	1.4227	1.4206	1.4186
Dodecyl ¹ ethanoate	1.4326	1.4306	1.4286	1.4265	1.4246
Tetradecyl ethanoate	1.4373	1.4352	1.4332	1.4312	1.4293
Hexadecyl ethanoate			1.4370	1.4350	1.4332
Octadecyl ethanoate				1.4381	1.4362

^a Accuracy ± 0.0001 .

Scott *et al.* (27) determined the refractive indices of the methyl esters of the saturated fatty acids from caprylic to stearic. The indices of refraction at 25°C. of methyl caprylate, caproate, laurate, and myristate were reported to be 1.4152, 1.4237, 1.4301, and 1.4351, respectively; and for methyl palmitate and stearate, 1.4327 and 1.4363, respectively, at 40°C.

The refractive indices of an extended series of carefully purified alkyl esters of aliphatic fatty acids from C₁ to C₁₂ and of the even-numbered carbon dibasic acids from C₂ to C₆ were reported by Vogel (36). These results are presented in Table 143. The refractive indices of several

TABLE 143
Refractive Index, $n_D^{20^\circ\text{C.}}$, of Alkyl Monoesters of Carboxylic and
Diesters of Dicarboxylic Acids (36)

Material	Methyl	Ethyl	<i>n</i> - Propyl	Iso- propyl	<i>n</i> - Butyl	Iso- butyl	<i>n</i> - Amyl	Iso- amyl
Formate		1.35983	1.37693	1.36783	1.38903	1.38546	1.39974	1.39700
Acetate	1.36193	1.37233	1.38442	1.37730	1.39406	1.39018	1.40228	1.40535
Propionate	1.37683	1.38394	1.39319		1.40101			
<i>n</i> -Butyrate	1.38729	1.39222	1.39950		1.40637		1.41226	1.41102
Isobutyrate	1.38299	1.38690	1.39552		1.40248			
Valerate	1.39690	1.40042	1.40672		1.41197		1.41635	
Isovalerate	1.39270	1.39621	1.40312		1.40875			
Caproate	1.40494	1.40712						
Heptanoate	1.41152	1.41286						
Caprylate	1.41696	1.41803						
Caprate	1.42556	1.42556	1.42797		1.43048			
Laurate	1.43188	1.43108	1.43350		1.43620			
Oxalate ^a		1.41023	1.41646	1.41281	1.42341		1.42887	1.42721
Succinate ^a	1.41951	1.41981	1.42521	1.41771	1.42992	1.42666	1.43425	1.43886
Adipate ^a	1.42832	1.42767	1.43143	1.42466	1.43525		1.43867	1.43712

^a Diester.

normal saturated fatty acids and their methyl and glyceryl esters, and of the corresponding alcohols were reported by Privett *et al.* (121); these data are collected in Table 144. For the refractive indices of some *n*-substituted amides of short chain fatty acids, see Vaughn and Sears (121a).

(b) Refractive Indices of Unsaturated Acids and Esters

Few data are available relative to the refractive indices of the unsaturated acids and esters. Wood *et al.* (122) reported the refractive indices of pure oleic, elaidic, linoleic, and linolenic acids at 50°C. to be 1.4487,

1.4468, 1.4588, and 1.4678, respectively. Hoerr and Harwood (50) give the refractive index of oleic acid as 1.4599 at 20°C. and 1.4564 at 30°C. For linoleic acid, these values are 1.4703 and 1.4664 at the same temperatures, respectively. Hawke (123) gives the value of 1.4703 as the refractive index of ricinoleic acid at 25°C.

TABLE 144
Melting Points and Refractive Indices of Normal Saturated Compounds (121)

Substance	Melting point (capillary method), °C.	Refractive index ^a
Caproic acid	-3.5	1.4170 ²⁰
Caprylic acid	16.2	1.4241 ³⁰
Capric acid	30.4	1.4287 ⁴⁰
Lauric acid	44.2	1.4328 ^{45.3}
Myristic acid	54.4	1.4329 ⁵⁵
Methyl caproate		1.3990 ³⁵
Methyl caprylate		1.4152 ²⁵
Methyl caprate		1.4239 ²⁵
Methyl laurate		1.4303 ²⁵
Methyl myristate		1.4350 ²⁵
Methyl palmitate	30.4-30.5	1.4359 ³⁵
Methyl stearate	38.5-38.9	1.4370 ⁴⁰
Caproyl alcohol	-47.7--47.2	1.4184 ²⁰
Caprylyl alcohol	-15.2	1.4292 ²⁰
Capryl alcohol	6.9	1.4372 ²⁰
Lauryl alcohol	24.5	1.4374 ²⁵
Myristyl alcohol	37.5	1.4347 ⁵⁰
Palmityl alcohol	49.3	1.4394 ^{51.5}
Stearyl alcohol	58.1	1.4390 ⁶⁰
Tricaproin		1.4431 ²⁵
Tricaprylin		1.4480 ²⁰
Tricaprin	29.0	1.4451 ⁴⁰
Trilaurin	43.0-43.5	1.4401 ⁶⁰
Trimyristin	54.0-55.0	1.4420 ⁶⁰
Tripalmitin	66.5	1.4387 ⁸⁰
Tristearin	70.0-71.0	1.4403 ⁸⁰

^a Superscript figure is the temperature (°C.) at which refractive index was measured.

McCutcheon (32,33) determined the refractive indices of ethyl linoleate and ethyl linolenate over the temperature range 23° to 60°C., with the results show in Table 145. The refractive indices for ethyl linoleate were measured with a butyrerefractometer with light filtered through a dichromate solution to approximate sodium light, while those for ethyl

linolenate were determined by means of an Abbe refractometer with sodium light.

TABLE 145
Refractive Indices of Ethyl Linoleate and Ethyl
Linolenate According to McCutcheon (32, 33)

Ethyl linoleate		Ethyl linolenate	
Temperature, °C.	Refractive index	Temperature, °C.	Refractive index
25.8	1.4578	23.0	1.4683
29.0	1.4565	30.2	1.4652
34.0	1.4546	33.6	1.4639
35.0	1.4542	38.0	1.4621
39.0	1.4526	43.7	1.4598
41.0	1.4518	47.6	1.4582
44.0	1.4505	60.0	1.4530
48.0	1.4489		
60.0	1.4443		

Values for the refractive indices obtained by Mattil and Longenecker (119) for methyl oleate, and for mixtures of methyl oleate–methyl linoleate and methyl linoleate–methyl linolenate, are included in Figures 42 and 43. Jackson *et al.* (124) reported the index of refraction of methyl linolelaidate to be 1.4562 and that of methyl linoleate as 1.4698 at 30°C. Privett *et al.* (121) determined the refractive indices of linolenic acid and the methyl and glyceryl esters of several unsaturated acids and the corresponding alcohols, with the results shown in Table 146.

TABLE 146
Refractive Indices of Unsaturated Acids and Derivatives (121)

Substance	Refractive index ^a
Linolenic acid	1.4805 ²⁰
Methyl oleate	1.4445 ⁴⁰
Methyl linoleate	1.4695 ²⁵
Oleyl alcohol	1.4580 ²⁵
Linoleyl alcohol	1.4676 ³⁰
Linolenyl alcohol	1.4778 ³⁰
Triolein	1.4638 ³⁰
Trilinolein	1.4750 ²⁵
Trilinolenin	1.4825 ⁴⁰

^a Superscript figure is the temperature (°C.) at which refractive index was measured.

(c) *Molecular Refractivity and Unsaturation*

It has been known for many years that when molecular refractivities are calculated from the atomic constants, adding in such constitutive factors as may be necessary, it is often found that an appreciable difference exists between the calculated value and the measured value calculated in terms of the Lorenz-Lorentz formula. This difference, called *molecular exaltation*, EM , has been traced to certain peculiarities in structure, and particularly to the presence of conjugated double bonds. Although the effect is evident in the refractive index and the density, it is magnified when expressed in molar terms. However, this multiplication may result in obscuring the effect in comparing compounds of different molecular weights. To avoid this difficulty it is customary to use *specific exaltation*, or $E\Sigma = 100(EM/m)$, where m is the molecular weight.

From the analysis of exaltation data, certain generalizations have been made relative to the effect of unsaturation on molecular refraction. One double bond in a compound produces no exaltation beyond that involved in the double bond increment used in calculating the theoretical molecular refraction. Two isolated double bonds in the compound likewise produce no abnormal exaltation. However, if the two double bonds are conjugated, a distinct exaltation is produced. The amount of the exaltation due to conjugation is, however, influenced by the length of the conjugated system, the presence of substituents, and branching of the conjugated chain. Exaltation increases as the length of conjugated chain increases, and is greatest for a linear conjugated system and decreases as the system becomes more branched.

Atomic and group refractions, obtained from data on hydrocarbons, may be used in calculating the Lorenz-Lorentz molar refraction of fatty acid esters, as reported by Tels and coworkers (124a). Using the equation,

$$r = A + B/M,$$

where r is specific refraction of the ester, M is molecular weight of the ester, and A and B are constants with the values of 0.3309 and -6.99 , respectively, these investigators calculated the value of r of several fatty acid esters and triglycerides and compared these values with those determined experimentally. The results are given in Table 146a.

The phenomenon of molecular exaltation should be especially significant in the study of polyunsaturated fatty acids, monoesters, and glycerides, and, particularly, in investigations involving shifts of isolated double bonds to conjugated positions. Actually, but little attention has been

TABLE 146a
Comparison of Observed and Calculated Specific
Refractions of Methyl Esters and Triglycerides (124a)

Methyl ester or triglyceride	r_D^{20} Observed	r_D^{20} Calculated	Deviation
Propionate	0.2516	0.2516	0.0000
Caproate	0.2772	0.2772	0.0000
Caprylate	0.2866	0.2867	+0.0001
Caprate	0.2933	0.2934	+0.0001
Laurate	0.2982	0.2983	+0.0001
Myristate	0.3022	0.3021	-0.0001
Oleate	0.3087	0.3088	+0.0001
Oleate	0.3090	0.3088	-0.0002
Petroselenate	0.3067	0.3088	+0.0021
Erucate	0.3123	0.3123	0.0000
Arachidonate	0.3135	0.3143	+0.0008
Tributyryl	0.2532	0.2523	-0.0009
Tricaproyl	0.2685	0.2694	+0.0009
Tricaprylin	0.2807	0.2804	-0.0003
Tricaprin	0.2885	0.2880	-0.0005
Trilaurin	0.2941	0.2937	-0.0004
Trimyristin	0.2987	0.2980	-0.0007
Tripalmitin	0.3021	0.3014	-0.0007
Tristearin	0.3044	0.3042	-0.0002

given to systematic studies of this type, and now that emphasis is being placed on absorption spectrophotometry, exaltation phenomena have lost considerable practical value in isomerization investigations.

8. Specific Conductivity

The electrical conductivity of any substance is its ability to carry an electric current or it is the reciprocal of its resistance. The resistance offered by conductors depends upon their nature and form; consequently, to compare the resistances of different substances they must possess the same form. Two such forms have been used, namely, a cube whose edge is one centimeter long, and a cylinder one meter in length and one square millimeter in cross section.

The conductance of a homogeneous substance of uniform cross section is proportional to its cross section, a , and inversely proportional to its length, l , i.e., $L = \lambda a/l$. The proportionality factor, λ , which is the conductance when the cross section is one square centimeter and the length one centimeter, is called the *specific conductance* and is the reciprocal of the *specific resistance*.

[illegible]

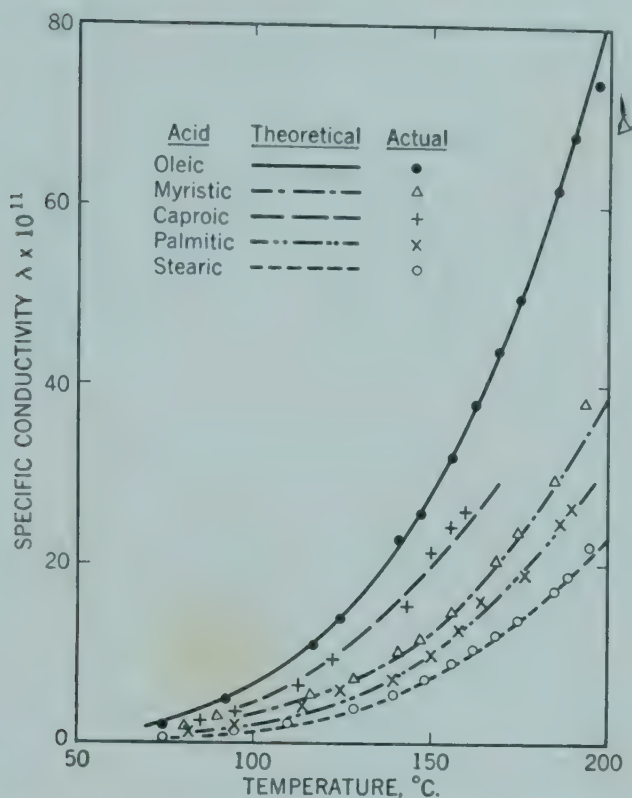


Fig. 44. Specific conductivity as a function of temperature for several fatty acids (125).

ture coefficients of conductivity can be determined. The specific conductivity decreases with increasing chain length in correspondence with the well-known decrease in the strength of the acids and corresponding ease of hydrolysis of their salts as the series is ascended.

The marked increase in conductivity of oleic acid compared with stearic acid is in accord with the known fact that the salts of unsaturated acids are more strongly dissociated and, therefore, better conductors than those of the saturated acids of the same chain length.

It has been observed that the curves for the temperature vs. the logarithm of the coefficient of electrical conductance of fused salts are generally linear in form. Lederer and Hartleb (125) found that this was only partly true for the fatty acids which they examined. When the logarithm of the conductivity was plotted against the temperature the curves (Fig. 45) were found to be linear up to about 140°C ., but above this temperature they tended to become concave to the temperature axis.

Lederer and Hartleb found that their data could be fitted to the equation $\ln \lambda = -a + bt - ct^2$ in which λ is the specific conductance and a , b ,

and c are constants having the values shown in Table 148 opposite the corresponding acid. By substituting for t the temperatures corresponding

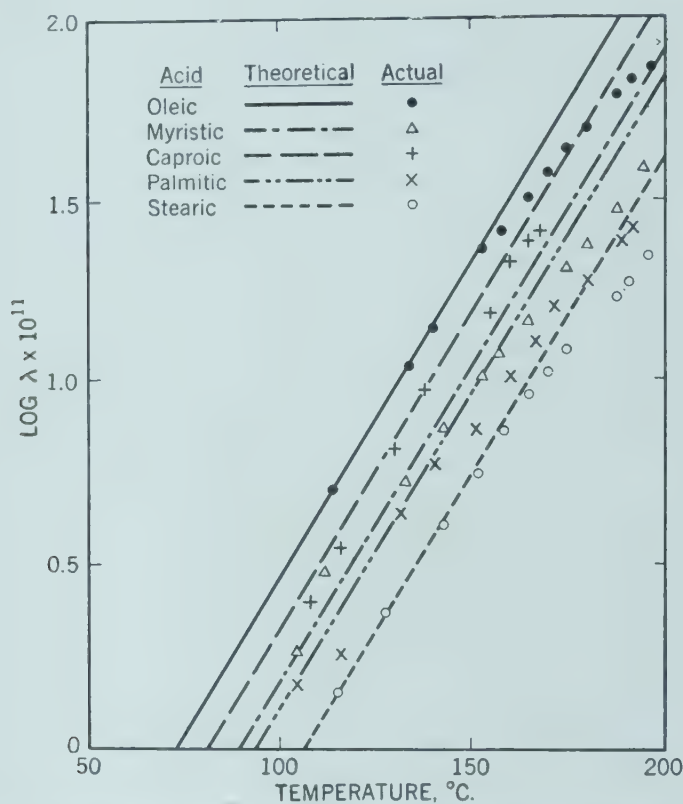


Fig. 45. Relation between the logarithm of the specific conductance and temperature of the higher fatty acids (125).

TABLE 148

Calculated Constants for Temperature Coefficient
Equation of Specific Conductance (125)

Acid	a	b	c
Caproic	13.007	0.0274	0.000042
Myristic	13.143	0.0278	0.000042
Palmitic	13.407	0.0281	0.000042
Stearic (tech.)	13.692	0.0289	0.000042
Oleic (tech.)	12.843	0.0275	0.000042

to the melting and boiling points of the acids, the specific conductances for these temperatures were found to correspond to those given in Table 149.

TABLE 149
Calculated Specific Conductivity for Several Fatty Acids
at Their Melting and Boiling Points (125)

Acid	$\lambda \times 10^{11}$ at m.p.	$\lambda \times 10^9$ at b.p.
Caproic	0.07	2.1
Myristic	0.16	1.7
Palmitic	0.15	1.9
Stearic	0.14	1.7
Oleic	0.03	2.8

9. Dielectric Constant

Dielectric constant is that property of a solid or liquid which, when the material is used as the dielectric medium in an electrical condenser, causes the capacitance of that condenser to be greater by some factor than when air is used as the dielectric in the same condenser. This property exhibits no molar relationship and may be expressed by an arbitrarily defined term, e.g., dielectric constant. The specific inductive capacity or dielectric constant, ϵ , is a function of the force f of repulsion between two point charges, e , e' , of electricity at a distance, r , apart in a uniform medium of great extent, i.e., $f = ee'/\epsilon r^2$.

The theory underlying this effect may be explained by stating that the molecules of substances align themselves in an electric field and so add the unbalanced electron charges existing in the molecule to the electron charges existing on the condenser plates. The greater the extent of their alignment and the greater their unbalanced electron charges, the higher will be the dielectric constant, therefore an increase in either viscosity or temperature tends to oppose this alignment. Increasing the temperature causes greater random distribution of the molecules. The higher the frequency of the current used, the more difficult it is for the molecules to follow the current reversals against the viscosity of the medium.

It should be mentioned that the dielectric strength, S , of a material is defined as the minimum value, in the material, of the electric field intensity, E , at which a disruptive charge occurs. In many cases it is doubtful if S is a constant, as it appears to vary with certain experimental conditions.

The dielectric constant may be determined by several methods, namely, from measurements of electrical capacities of mechanical forces between charged conductors, or of the wave lengths of electrical waves. Hazle-

hurst (126) has described a simple apparatus and a method for determining the dielectric constants of fats and oils. The test cell consists of a brass bar 0.75 in. in diameter and 13 in. long, insulated from, and held concentric within, a brass tube 1 in. in inside diameter, together with the necessary end caps and means for making electrical contact. This device is constant in capacitance, and is easily dismantled and cleaned. The cell must be accurately checked for replacement capacitance, that is, the area that is filled by the liquid under test, and since the dielectric constant of pure benzene has been accurately determined it can be used as the standardizing medium. There is also required a precision variable condenser, a special Shering-type bridge, a.c. voltage sources covering the desired frequency ranges, and bridge balance detectors. These items of equipment are all standard and can be purchased from instrument manufacturers. According to Hazlehurst, a temperature of 30°C. and for most purposes a frequency of 200 kilocycles per second are satisfactory for making dielectric measurements.

At one time considerable interest was evinced in the dielectric constants of the fatty acids and the corresponding esters. During the 1890's a considerable number of papers appeared with reference to the dielectric constants of the lower members of the fatty acid series (formic to caprylic), and of the corresponding methyl, ethyl, propyl, butyl, isobutyl, and amyl esters. Many such measurements were reported prior to 1900 by Drude (127), Löwe (128), Jahn and Möller (129), Tereschin (130), Linebarger (131), Landolt and Jahn (132), and others. Between 1910 and 1925, Dobroserdov (133), Jackson (134), Grimm and Patrick (135), and others reported the results of new determinations on many of these same acids and esters.

Wirth and Wellman (139) determined the dielectric constant of hydrous sodium palmitate in two polymorphic forms. The ϵ of the β -form of sodium palmitate was constant at 2.61 ± 0.02 for moisture contents between 1.38 and 3.00%. For the δ -form of sodium palmitate, the value found was 2.51 with 0.15% of water to 2.95% of water present. Both values were independent of the frequency used in measuring the dielectric constants.

Although there is a considerable accumulation of data with reference to the dielectric constants of the lower members of the fatty acid series, those for the higher members are much less extensive. Kahlenberg (138) determined the dielectric constants of oleic acid and a number of its metallic salts. Three samples of reagent-grade oleic acid were measured at 20°C. and the dielectric constants were found to be 2.50, 2.57, and 2.60.

The dielectric constants for the corresponding salts at 20°C. were: ferric, 2.68; aluminum, 2.40; copper, 2.80; sodium, 2.75 to 2.83; and lead, 3.27 at 18°C. and 3.70 at the melting point.

The dielectric properties of some aluminum soaps of fatty acids in toluene solution were investigated by Nelson *et al.* (138a), who found that gels were formed at low concentrations. Dielectric loss in such gels is caused by restricted displacement and accumulation of ions along internal boundaries in the gel.

Hrynakowski and Zochowski (136), in a careful study of the association of various fatty acids in benzene, also determined the dielectric constant of these acids. Their results, together with those of (127) for the lower acids and of Lautsch (137) for stearic acid are given in Table 150.

TABLE 150
Dielectric Constants of Some Fatty Acids (127,136,137)

Acid	Temperature, °C.	Dielectric constant
Formic	2	19.0
Acetic	19	6.29
Propionic	17	3.15
<i>n</i> -Butyric	17	2.70
<i>n</i> -Valeric	20	2.67
<i>n</i> -Caproic	71	2.632
Heptanoic	71	2.587
<i>n</i> -Caprylic	71	2.544
Palmitic	71	2.348
Stearic	71	2.318
	67	2.32
	100	2.26

Kahlenberg examined a number of natural oils (olive, 2.60; corn, 2.50; cottonseed, 2.30) having a high content of oleic acid and found that the free acid and oils had relatively similar values. In view of the presence of a carboxyl group and a double bond in oleic acid, he considered the dielectric constant of this acid to be abnormally low. He also stated that it was curious that the specific inductive capacity of oleic acid was so slightly changed by the introduction of heavy metals. It is possible that the dielectric constants observed by Kahlenberg were due to the poor quality of oleic acid which was available at the time (1905) that these measurements were made.

Bogdanov and Stepanenko (140) determined the dielectric constants of linolenic acid and of tripalmitin with the results given in Table 151. Morgan and Yager (141) and Lautsch (137) reported the dielectric constants for a large number of organic compounds including several esters

TABLE 151
Dielectric Constants of Linolenic Acid and Tripalmitin (140)

Compound	Temperature, °C.	Dielectric constant, ϵ
Linolenic acid	-10	2.55
	20	2.76
	60	2.97
	100	3.01
Tripalmitin	-45	2.272
	-30	2.354
	-6	2.402
	5	2.444
	20	2.544
	55	2.901
	80	2.954
	120	2.924

of fatty acids, which latter are assembled in Table 152. Morgan and Yager concluded that the dielectric constants of the esters of fatty acids are not large, ranging from 6 to 7 for esters of lower molecular weight, such as methyl and ethyl acetate, to 3 to 4 for the esters of long-chain fatty acids such as butyl stearate and oleate.

The dielectric constants of a few other alkyl esters are to be found in the literature, e.g., Walden (142) reported the dielectric constant of isobutyl ricinoleate to be 4.7 at 21°C. Crowe and Smyth (143) in an investigation of orientation, measured the dielectric constants of some alkyl esters of palmitic and stearic acids at various frequencies and temperatures. These values at 5 kilocycles were found to be: *n*-hexadecyl palmitate, 2.940 at 19.8°C.; *n*-deeryl palmitate, 3.078 at -2.0°C.; *n*-dodecyl stearate, 3.063 at 20.5°C. The high dielectric constants of the solid state indicates probable dipole orientation about the long axis for *n*-deeryl palmitate and *n*-dedecyl stearate. For dielectric properties of *n*-substituted amides of the short chain fatty acids, see Vaughn and Sears (121a).

Because of the anomalous transitions exhibited by ethyl behenate,

TABLE 152
Dielectric Constants of Several Fatty Acid Esters (137,141)

Ester	Dielectric constant, ϵ	Temperature, °C.
Methyl acetate	6.7	25
Ethyl acetate	6.15	20
Bornyl acetate	4.6	21
Ethyl laurate	3.44	20
	3.16	60
	2.91	101
	2.73	143
Ethyl palmitate	3.07	30
	2.88	69
	2.71	104
	2.57	144
	2.46	182
Ethyl stearate	2.92	48
	2.69	100
	2.56	138
	2.48	167
Butyl stearate	3.30	25
Ethyl oleate	3.17	28
	3.00	60
	2.87	89
	2.72	122
	2.63	150
Butyl oleate	4.0	25
Glyceryl triacetate	9.4	24

Buckingham (144) determined the dielectric constant, density, and molecular volume of ethyl behenate in the liquid and solid states. The results of the dielectric constant measurements were expressed in the form of graphs in which the dielectric capacity was plotted against temperature. From the changes in the dielectric capacity and density between the melting point and room temperatures, Buckingham concluded that this ester exists in at least four polymorphic modifications which he designated α_1 , α_2 , β_1 and β_2 . The α_1 -form was metastable but could be observed between 45°C. and the melting point, and could be produced by cooling a melt. At 45°C. it was found to pass irreversibly into the α_2 -form which was also metastable but could be examined between 43°C. and the melting point. At 43°C. the α_2 -form passed to the β_1 -form which in turn passed reversibly to the β_2 -form at 30°C. The

inversion of the α_2 -form to the β_1 -form was accompanied by marked changes in the density, polarization, x-ray spacing, and energy content. The changes from α_1 to α_2 , and from β_1 to β_2 were not accompanied by abrupt alteration of these properties.

Very few dielectric constants have been reported for the glyceride esters of fatty acids. Crowe and Smyth (145) investigated the dielectric properties of monostearin and monopalmitin over a considerable range of frequency and temperatures, as may be seen from Table 153. The dielectric constant of monopalmitin was observed to increase normally in the liquid state until the freezing point of the α -form was reached at 66°C., beyond which it increased sharply. Monostearin exhibited the

TABLE 153
Dielectric Constants of 1-Monoglycerides (145)

Phase	Temperature, °C.	Frequency, kc.			
		100	50	25	5
1-Monopalmitin					
Liquid	80.1	5.09	5.09	5.09	5.09
	67.1	5.34	5.34	5.34	5.34
α	65.7	6.26	7.13	9.15	22.10
	53.2	5.75	6.33	7.54	14.36
Sub- α	31.4	4.95	5.00	5.08	5.63
	-36.9	2.38	2.40	2.42	2.53
β	57.1	2.60	2.69	2.91	3.98
	47.2	2.53	2.61	2.71	3.18
1-Monostearin					
Liquid	89.1	4.71	4.71	4.72	4.73
	77.1	4.87	4.87	4.87	4.88
α	72.1	5.82	6.80	8.90	22.20
	50.2	5.15	5.48	6.20	10.73
Sub- α	32.4	4.41	4.46	4.50	4.84
	-24.5	2.53	2.62	2.71	3.03
β	71.1	2.64	2.80	3.03	4.37
	43.2	2.53	2.58	2.69	3.13

same general behavior. These workers also determined the dielectric constant of di- and tripalmitin and di- and tristearin, which they related

to determine the polymorphism of these glycerides. Their results are given in Table 154.

TABLE 154
Dielectric Constants of Glycerides at a Frequency of 5 Kc. (145)

Phase	Temperature, °C.	ϵ	Phase	Temperature, °C.	ϵ
<i>1,3-Dipalmitin</i>			<i>1,3-Distearin</i>		
Liquid	76.0	3.49	Liquid	82.0	3.29
	72.0	3.52		78.0	3.32
β -a	26.5	2.50	β -a	21.5	2.40
	60.1	2.55		70.1	2.43
β -b	44.2	2.55	β -b	14.7	2.39
	64.1	2.57		68.6	2.44
<i>Tripalmitin</i>			<i>Tristearin</i>		
Liquid	70.0	2.895	Liquid	80.0	2.751
	60.0	2.927		70.0	2.785
α -Form	-140.0	2.327	α -form	-147.0	2.283
	41.3	2.737		52.2	2.684
β -Form	20.6	2.292	β -form	16.7	2.313
	60.0	2.320		65.1	2.340

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CHAPTER VII

SOLUTION PROPERTIES

W. S. SINGLETON

New Orleans, Louisiana

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1. Introduction

A solution may be defined as a homogeneous mixture of various molecular species or as a one-phase system consisting of two or more molecular species. Pairs of substances that are capable of forming solutions when brought in contact do so to very different degrees, depending on the nature of the two substances and the conditions under which they are mixed. For example, at some specified temperature, water and acetic acid may be miscible in all proportions, whereas water and stearic acid may be almost immiscible.

When two substances are mixed to form a solution, one component is referred to as the solvent and the other as the solute. In the case of solutions of two liquids either component may be considered as the solvent. For example, at $-3^{\circ}\text{C}.$, a mixture of water and butyric acid will contain 39.5% of butyric acid and the water may be considered as the solvent, whereas a mixture of caproic acid and water at $46^{\circ}\text{C}.$ will contain 9.7% of water and caproic acid may be considered as the solvent.

Solutions in general, and so-called ideal solutions in particular, exhibit the same interrelationships between colligative properties—vapor pressure, boiling points, freezing points, etc.—as are exhibited by pure liquids, and they are amenable to the same type of thermodynamic treatment, although the effect of changing concentrations complicates their quantitative treatment. Besides colligative properties, solutions possess other properties, such as refractive index, viscosity, conductivity, etc., which are of importance in evaluating or utilizing the systems comprising such mixtures. In the act of mixing two substances, physical phenomena involving changes in heat content, volume, density, etc., occur which may be of considerable magnitude and importance, especially when such processes are carried out on a large scale.

The investigation of the solubility relationships and the properties of solutions forms one of the most important fields of physical chemical research, and one which has received a vast amount of attention over a period of many years. However, prior to the early 1940's, little of the work in this field was directed toward the fatty acids, and particularly the higher fatty acids. This was probably due in part to the relatively low solubility of these substances in water and the fact that organic solutions are more difficult to investigate than are aqueous types. Only since about 1940, and primarily through the efforts of relatively few groups of workers, has our knowledge of the solubilities of the fatty acids and related compounds (alcohols, esters, ketones, amines, amine salts, anilides, and diphenylamides) been placed in a position comparable with other less important homologous series of organic compounds.

An interpolative method of calculating the solubilities of those members of homologous series for which some data are missing was reported by Skau and Boucher (1). The linear equation

$$\log N = a + bn$$

was derived from the approximate freezing point lowering equation and the known empirical relationships between the number of carbon atoms and the heats and entropies of fusion of the members of a homologous series. In the derived equation, N is the solubility of a homolog expressed in mole % ($100 N$) in a given solvent at a given temperature, a and b are constants which depend on temperature and the system involved, and n is the number of carbon atoms in the dissolved compound. Log N vs n isotherms were plotted for 125 systems, involving 10 homologous systems in 16 different solvents, utilizing published data for known members of homologous series, and the results presented in tabular form. The actual

solubility charts are presented in another publication by these same authors (1a). Included were fatty acids, methyl esters of the fatty acids, ketones, alcohols, amides, amines and other compounds in solvents such as benzene, cyclohexane, carbon tetrachloride, chloroform, and others. By graphical interpolation, the isotherms make it possible to predict the solubility of an unknown member, the precision depending upon the accuracy and consistency of the original data, and upon the amount and type of curvature of the isotherms. For example, the published solubility data for the homologous symmetrical aliphatic secondary amines include only those members having 16, 24, 26, 28, 30 and 36 carbon atoms. It was possible from the plotted isotherms to read off the solubilities of those members containing 18, 20, 22, 32 and 34 carbon atoms.

This interpolative method may also be used to smooth out experimental solubility data, and to locate the discrepancies caused by experimental error. For example, the solubility of myristic acid in absolute methanol was determined and found to be 2.99 mole % at $20.4 \pm 0.2^\circ\text{C}$., which is in better agreement with the isotherm for the system than the reported value of 2.37 mole % at 20°C .

The isotherm method has been supplemented by the isopleth method, which was developed by Skau and Bailey (1b) to predict the solubilities in mole % of several hydrocarbons and normal aliphatic compounds including fatty acids containing 11, 13 and 19 carbon atoms, and the fatty acid methyl esters containing 11 and 21 carbon atoms. The isopleth method is based upon the linear relationship,

$$1/T = a(1/n + b),$$

derived from the approximate freezing point depression equation and empirical relationships between the number of carbon atoms, n , and heats and entropies of fusion of the members of a homologous series. T is absolute temperature at which saturated solutions of the various homologs in a given solvent contain the same mole fraction of solute; the coefficients a and b are constants. The predicted solubility temperatures of some fatty acids and fatty acid esters in hexane are given in Table 154a. The combined use of the isopleth and isotherm methods of correlation makes it possible to obtain similar solubility data for other solvents and other homologous series on the basis of a minimum of experimental measurements.

The data with reference to solubility determinations may be expressed in several ways and the choice of the mode of expression is generally dependent on the use which is to be made of the results. Data collected in

solubility tables are generally expressed as grams of solute in one hundred milliliters of solvent at a specified temperature, usually 20°C. Another method is to express the composition on a weight-per cent basis, i.e., on the basis of the number of grams of solute which are soluble in one hundred grams of solvent. Although the latter method is preferable in many instances, it is not convenient for use in investigations of the colligative properties of solutions which are dependent upon the relative number of molecules present in the solution rather than upon the relative weights of the substances present. In this case it is necessary to express composition in terms of gram-molecular weights or mole fractions, i.e., in moles, equivalents, or formula weights per liter of solution or per one thousand grams of solvent.

TABLE 154a

Predicted Solubility Temperatures (°C.) of Some *n*-Saturated Fatty Acids and Esters in *n*-Hexane (1a)

No. carbon atoms	Mole %					
	80	60	40	20	10	6
<i>Odd saturated fatty acids</i>						
19	65.3	60.6	55.8	49.0		
13	35.8	31.0	25.9	19.2		
11	22.7	17.4	11.9	4.5		
<i>Methyl esters of even saturated fatty acids</i>						
21	42.6	40.0	36.3	29.2	23.4	19.7
11	-11.7	-15.0	-19.4	-25.6	-31.5	-35.6

After converting solubility data obtained from various sources and expressed in different manners to a single and comparable basis, some method must be applied to determine their relative accuracy or reliability and hence their utility. One such method comprises plotting the logarithm of the mole fraction of solute against the reciprocal of the absolute temperature. This method was employed by Hildebrand and Scott (2) with a number of substances and by Bailey to evaluate the solubilities of fatty acids and their derivatives (3). Such plots permit comparison of solutes on a molar basis and, in general, indicate the degree of reliability of the data in terms of the relative deviation from ideality.

By way of explanation of this method of representing solubility data, Bailey states, "Often, in dealing with fatty compounds of relatively low solubility and high molecular weight, it is satisfactory simply to plot the solubility in terms of grams per 100 grams of solvent or solution on the

logarithmic coordinate and the temperature in degrees C. or F. on the linear coordinate. Over short temperature intervals relative values of T and $1/T$ are usually not very different, and in the lower ranges of solubility there is usually similar close correspondence between relative values of solubility expressed in terms of mole fractions of solute and solubility expressed in the more usual way."

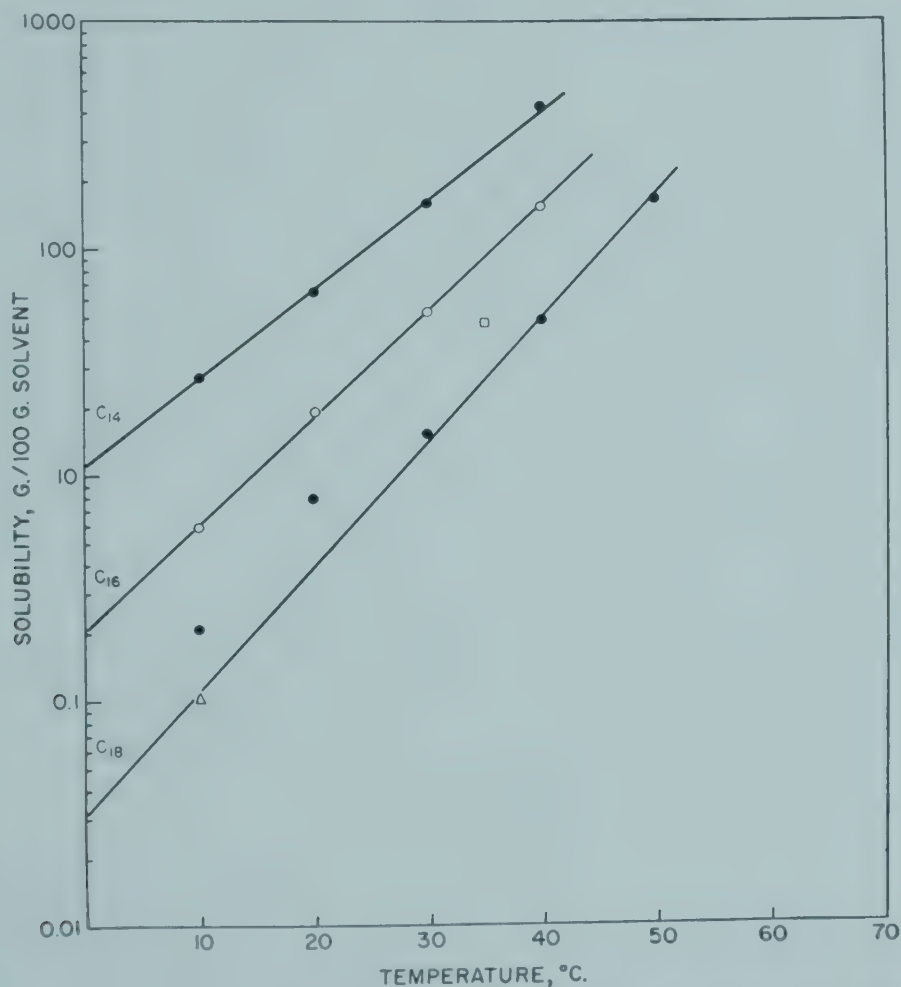


Fig. 46. Solubilities of myristic, palmitic, and stearic acids illustrating simplified method of plotting results (3).

Figure 46 is representative of the simple type of plot (g./100 g. solvent vs. temperature) for the solubility of myristic, palmitic, and stearic acids in acetone and Figure 47 of the plot of the solubility of the mole fraction

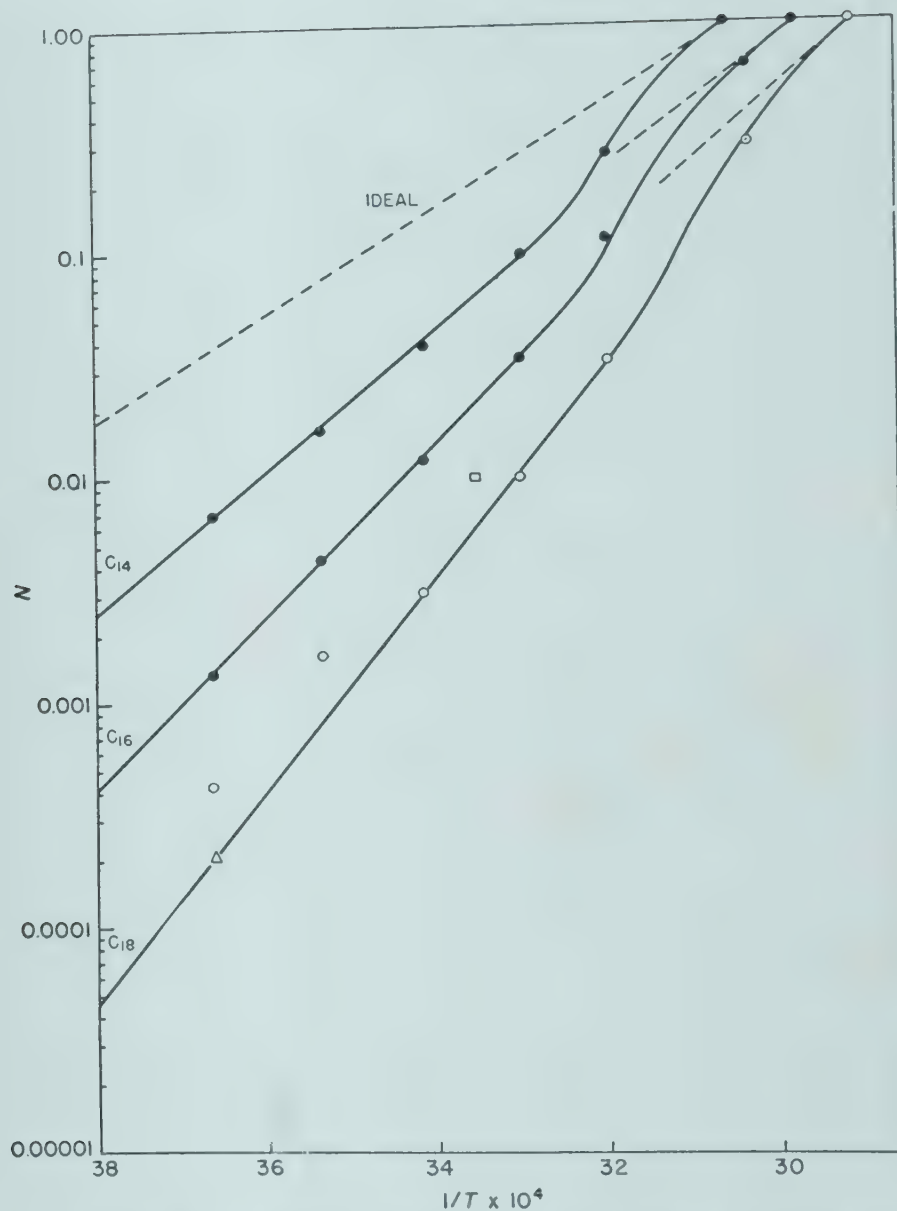


Fig. 47. Solubilities of myristic, palmitic, and stearic acids in acetone illustrating preferred method of plotting (3). Values plotted as circles are those of Hoerr and Ralston (4). Value plotted as a triangle is from Singleton (5). Value plotted as a square is from Seidell (6).

vs. the reciprocal temperature for the same acids. The latter figure is a good example of the use of this type of plot for determining the validity or reliability of experimental values. Singleton (5) found the solubility of

carefully purified stearic acid to be 0.103 g. per 100 g. of acetone at 0°C. In the figure, this value falls on the same line with the data of Hoerr and Ralston (4) except for their two lowest values (0° and 10°C.) which apparently are in error.

2. Miscible Aqueous Systems

(a) Solutions of Fatty Acids and Water

The fact that the normal fatty acids exhibit appreciable solubility in water compared to the corresponding hydrocarbons is due to the presence in the former of the polar or hydrophilic carboxyl group. The lowest molecular weight hydrocarbons are slightly soluble in water at room temperature, but their solubility decreases rapidly as the carbon chain increases and above C_8H_{18} they are practically insoluble. In contrast to the hydrocarbons, the first four members of the saturated fatty acid series are miscible with water in all proportions at room temperature; even valeric acid, C_4H_9COOH , is soluble to the extent of 3.7 g. per 100 g. water.

These relations are emphasized by the solubility values for the first seven normal hydrocarbons and those of the corresponding acids shown in Table 155. It is evident from the data in Table 155 that, as the hydro-

TABLE 155
Solubility of Normal Hydrocarbons and Corresponding Fatty
Acids in Water at 20°C. (except as otherwise indicated)

Hydrocarbon			Acid		
Name	Formula	g./100 g.	Name	Formula	g./100 g.
Ethane	CH_3CH_3	4.7 cm. ^{3a}	Acetic	CH_3COOH	∞
Propane	$CH_3CH_2CH_3$	6.5 ^{18°} cm. ^{3a}	Propionic	CH_3CH_2COOH	∞
Butane	$CH_3(CH_2)_2CH_3$	15 ¹⁷ ₇₂ °	Butyric	$CH_3(CH_2)_2COOH$	∞
Pentane	$CH_3(CH_2)_3CH_3$	0.036 ^{16°}	Valeric	$CH_3(CH_2)_3COOH$	3.7
Hexane	$CH_3(CH_2)_4CH_3$	0.0138 ^{15.5°}	Caproic	$CH_3(CH_2)_4COOH$	0.9
Heptane	$CH_3(CH_2)_5CH_3$	0.0052 ^{15.5°}	Heptanoic	$CH_3(CH_2)_5COOH$	0.24
Octane	$CH_3(CH_2)_6CH_3$	0.0015 ^{1°}	Caprylic	$CH_3(CH_2)_6COOH$	0.07

* Cubic centimeters rather than grams because material is gas.

carbon chain increases, the ability of the carboxyl group to bring about solubility of the acid in water becomes decreasingly effective. As will be shown later, its ultimate effect will be merely to orient the fatty acid with respect to a water surface.

Ralston and Hoerr (7) reported the results of a systematic investigation of the solubility in water of the normal fatty acids from caproic to stearic at various temperatures between 0° and 60°C. Their results are

TABLE 156
Solubilities of Fatty Acids in Water (7)

Acid	Grams acid per 100 g. water				
	0°C.	20°C.	30°C.	45°C.	60°C.
Caproic	0.864	0.968	1.019	1.095	1.171
Heptanoic	0.190	0.244	0.271	0.311	0.353
Caprylic	0.044	0.068	0.079	0.095	0.113
Nonanoic	0.014	0.026	0.032	0.041	0.051
Capric	0.0095	0.015	0.018	0.023	0.027
Hendecanoic	0.0063	0.0093	0.011	0.013	0.015
Lauric	0.0037	0.0055	0.0063	0.0075	0.0087
Tridecanoic	0.0021	0.0033	0.0038	0.0044	0.0054
Myristic	0.0013	0.0020	0.0024	0.0029	0.0034
Pentadecanoic	0.00076	0.0012	0.0014	0.0017	0.0020
Palmitic	0.00046	0.00072	0.00083	0.0010	0.0012
Heptadecanoic	0.00028	0.00042	0.00055	0.00069	0.00081
Stearic	0.00018	0.00029	0.00034	0.00042	0.00050

reproduced in Table 156. Ralston *et al.* (8) also determined the effect of the addition of water on the depression of the freezing point of the same series of fatty acids, with the results shown in Figure 48. Reference to

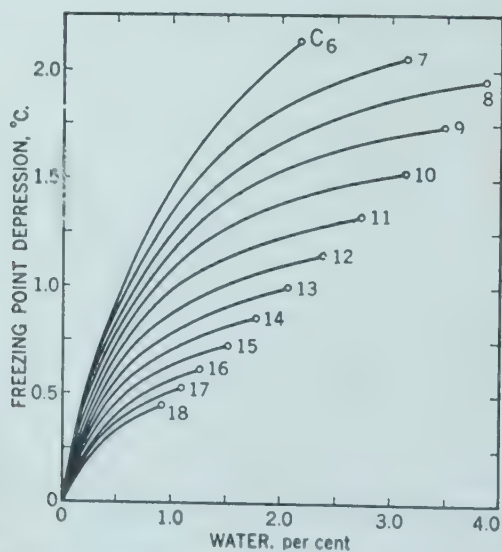


Fig. 48. Effect of addition of water on the freezing point of the fatty acids from C₆ to C₁₈ (8).

the curves of Figure 48 indicates that the maximum depression for any given acid is greater than that of the next higher member of the series; also that the maximum lowering of the freezing point varies from approximately $2^{\circ}\text{C}.$, in the case of caproic acid containing 2.2% of water, to approximately $0.5^{\circ}\text{C}.$ for stearic acid saturated with water.

Eggenberger *et al.* (9) reinvestigated the solubility of the saturated acids C_8 to C_{12} and C_{14} in water and found them to be less soluble than indicated by the values in Table 156. For example, at $60^{\circ}\text{C}.$ the solubilities in grams per 100 cc. solution were reported to Eggenberger *et al.* to be caprylic, 0.1071; pelargonic, 0.0299; capric, 0.0100; hendecanoic, 0.0032; lauric, 0.00116; and myristic, 0.00056. It should be noted that these values are expressed as grams per 100 cc. of solution, whereas the values in Table 156 are expressed in grams per 100 g. of water.

The last-mentioned authors also determined the approximate solubilities of water in fatty acids at various temperatures and computed those of the undetermined systems, with the results shown in Table 157. From the

TABLE 157
Approximate Solubilities of Water in Saturated
Fatty Acids at Various Temperatures (8)

Acid	Temp., $^{\circ}\text{C}.$	Water, %	Acid	Temp., $^{\circ}\text{C}.$	Water, %
Caproic	-5.4	2.21	Lauric	42.7	2.35
	12.3	4.73		75.0	2.70
	31.7	7.57		90.5	2.85
	46.3	9.70	Tridecanoic	40.8	2.00
Heptanoic	-8.3	2.98	Myristic	53.2	1.70
	42.5	9.98		51.8	1.46
Caprylic	14.4	3.88	Palmitic	61.8	1.25
Nonanoic	10.5	3.45		60.4	1.06
Capric	29.4	3.12	Heptadecanoic	68.7	0.92
	26.8	2.72		92.4	1.02
Hendecanoic	57.5	4.21	Stearic		

data in this table it may be seen that increasing the temperature increases the solubility of water in the acids of low molecular weight, but in the case of the higher members it has only a very small effect.

Water is partially soluble in a pure molten monoglyceride; Brokaw and Lyman (9a) found that as water is added to monoolein in an amount of about 10 to 15% by weight, the viscosity of the monoolein increased to a soft transparent "solid." As further water is added, the solid becomes firmer until no more water can be incorporated. The "gel point" of several monoglycerides are given in Table 157a.

TABLE 157a
Gel Points of Monoglycerides (9a)

Monoglycerides ^a	M.p., °C.	"Gel point," °C.
Distilled monolaurin	54-57	No gel to 99
Distilled monomyristin	62-65	85
Distilled monopalmitin	67-68	68
Distilled monostearin	70-72	70
1-Monomyristin	70.5	No gel to 99
1-Monopalmitin	74-74.5	82
1-Monostearin	81-81.5	81
Distilled monoolein	35	<20

^a Distilled products usually contain about 90-92% 1-monoglyceride, 5-8% of 2-monoglyceride, and 1-3% of glycerine, diglycerides, and free fatty acids. (G. Y. Brokaw, E. S. Perry, and W. C. Lyman, *J. Am. Oil Chem Soc.*, **32**, 194-197 (1955)).

(b) Dissociation and Electrical Conductance

Solution of a fatty acid in water is accompanied by dissociation of the molecule into ions in a manner analogous to inorganic acids. The acidic properties, or the ionizable hydrogen of all the fatty acids, have their origin in the same portion of the molecule, namely, the carboxyl group. While the hydrogen of the carboxyl group is as replaceable by metals as that of organic acids, dissociation of fatty acids in aqueous solution occurs to a much smaller degree than is the case with strong mineral acids.

The degree of dissociation of an acid and its relative strength is expressed as the dissociation constant. This constant, which is derived from the dilution law, relates the degree of dissociation of a weak acid and its dilution. If, in the case of the fatty acids which are dissociated as follows:



it is assumed that one gram mole of the acid is dissolved in y liters of water, and x gram mole is dissociated, then the concentration of ions is x/y and that of the undissociated acid $(1 - x)/y$, and from the law of mass action under equilibrium conditions:

$$\frac{\{[H]^+[C_nH_{2n+1}COO^-]\}}{[C_nH_{2n+1}COOH]} = \frac{(x^2/y^2)/[(1 - x)/y]}{= k = x^2/[y(1 - x)]}$$

The values of k for the normal fatty acids have been determined only for the series formic to nonanoic, because the solubility of the acids in water is very slight with chain length above C_9 .

Closely related to the dissociation of fatty acids into ions is the electrical conductance of their solutions. In fact, the conductance of such solutions serves as a measure of the degree of dissociation of the dissolved acids (10). These relationships are emphasized by the values for the dissociation constants and equivalent conductances of the acids shown in Table 158. From this table it may be seen that formic acid undergoes

TABLE 158
Dissociation Constants and Equivalent Conductances for
Normal Fatty Acids in Aqueous Solutions at 25°C.^a

Acid	Dissociation constant, $k \times 10^5$	Equivalent conductance, Λ_0
Formic	21.0	404
Acetic	1.813	390.8
Propionic	1.32	386
Butyric	1.50	383
Valeric	1.56	381
Caproic	1.40	379
Heptanoic	1.30	378
Caprylic	1.41	377
Nonanoic	1.1	377

^a J. Kendall, in *International Critical Tables*, Vol. VI, McGraw-Hill, New York, 1929, pp. 259-304.

dissociation to an extent about ten times greater than acetic acid. Acetic acid has a dissociation constant of 1.8×10^{-5} and is, therefore, a weak and sparingly dissociated acid. A 1 M aqueous solution is dissociated only to the extent of 0.4% compared to the strong mineral acids which are completely ionized in dilute solutions. Tenth normal acetic acid is only about one-hundredth as much dissociated at 0.1 N hydrochloric acid, that is—it is only one-hundredth as strong as hydrochloric acid.

Propionic acid is even more feebly ionized and as the series is ascended the dissociation constants and equivalent conductances decrease but slightly. Although all of these acids are feebly acidic, they are stronger than carbonic acid ($k_1 = 3.4 \times 10^{-7}$). The relative dissociation constants of the fatty acids indicate that they will be liberated from their alkali salts by hydrochloric acid, and that they in turn will liberate carbonic acid from sodium bicarbonate.

The degree of dissociation is often affected appreciably by temperature, but in the case of the fatty acids variation of the value of the dissociation constant with temperature is small.

The alkali salts of the very weakly dissociated higher fatty acids are always considerably hydrolyzed in aqueous solution, and as a result their solutions react alkaline as indicated by the equation:



The normal aliphatic acids, or at least the lower members which have been investigated, are strongly associated, and at temperatures just above their boiling points have molecular weights twice the molecular weight corresponding to their empirical formulas. Because of the tendency of the fatty acids to exist as dimers they are capable of forming salts of the formula: $C_nH_{2n+1}COONa \cdot C_nH_{2n+1}COOH$ (see Chapter VIII).

Substitution of various substituents, especially halogens and hydroxyls, for hydrogen in the methylene chain markedly affects the dissociation constant of the resultant acid. The most marked effect occurs when the substitution takes place in the methylene group nearest the carboxyl, and decreases with increasing distance from this group. The effect of substitution of various atoms and radicals on the dissociation constant of fatty acids is illustrated in Table 159.

TABLE 159
Effect of Substitution and Position of Substituent on
Value of Dissociation Constant ($k \times 10^6$) of Fatty Acids

Substituent	Acetic α	Propionic		Butyric			Valeric δ
		α	β	α	β	γ	
None	1.85	1.32	1.32	1.53	1.53	1.53	1.59
Methyl	1.32	1.48	1.53	1.69	1.67	1.59	1.46
Chlorine	147.0	160.0	8.59	140.0	8.85	2.96	2.0
Bromine	132.0	106.0	9.3	102.0		2.61	1.88
Iodine	70.0		8.6			2.26	1.68
Hydroxyl	15.0	13.6	3.07	31.0		1.90	1.32
Sulphydryl	22.5						

The α,ω -dibasic acids are both more soluble and more extensively dissociated than the corresponding monobasic acids. Since the dibasic acids contain two carboxyl groups, both of which yield hydrogen ions, they have two dissociation constants, k_1 and k_2 , of which the former is very much greater than the latter.

3. Immiscible Aqueous Systems

It was mentioned previously that the solubility of the normal fatty acids in water resulted primarily from the presence of the carboxyl group in the otherwise insoluble or slightly soluble hydrocarbon chain of these compounds. It was also mentioned that, as the hydrocarbon chain increased in length, the effectiveness of the carboxyl group in producing solubility of the acids diminished almost to the vanishing point. It will now be seen that even when the carboxyl group is relatively incapable of effecting solution it may still influence the behavior of a water-acid interface to produce oriented mono- and polymolecular films.

(a) Monomolecular Films

Nature of Monomolecular Films. When a drop of an immiscible animal or vegetable oil, fatty acid, oxidized paraffin hydrocarbon, fatty acid ester, higher alcohol, ketone, nitrile, amide, or other polar or semipolar substance is placed on water it spreads to form a thin uniform layer. Investigation of the properties of these films by means of the film balance has led to important discoveries concerning the forces between the molecules, the cross-section area of packed molecules, orientation of surfaces, and other related properties.

Several theories have been advanced relative to the spreading of oil films on water. The theory of Langmuir (11) is perhaps the simplest and most applicable to the naturally occurring fats and oils and their derived products. According to Langmuir's theory, nonpolar liquids, such as the hydrocarbons, do not spread on water, but if the molecules contain a polar or *hydrophilic* group and a nonpolar or *hydrophobic* group, the liquid will spread. Furthermore, most of the films formed in this manner are only one molecule thick and for any given substance have all their molecules similarly oriented, often simply perpendicular to the surface and parallel to each other.

Investigation has revealed the fact that the molecules of these oriented films are arranged so that their polar (hydrophilic) portions, which possess an affinity for water, go into solution while the insoluble (hydrophobic) portion tends to float above the surface of the water. Oriented films of this type exhibit various properties which can be qualitatively observed and quantitatively measured. For example, they are subject to mechanical compression which produces several readily observable effects. A thin film of colorless mineral oil such as Nujol when placed on a clean surface of water does not spread, but if the oil is first slightly

oxidized it spreads as a uniform polymolecular film. If the expanded film is subjected to compression by a movable barrier, it will exhibit a series of colors (yellow, gold, red-purple, blue, and green) as the compression is increased. On further compression the color spectrum will be repeated four or more times until a limiting compression value is reached when the film again becomes colorless.

Measurement of Monomolecular Films. The effect of this compression can be measured quantitatively by means of the film or hydrophil balance. The film balance is a relatively simply device by means of which considerable quantitative information can be obtained concerning the nature of the material composing the film. One type of film balance (Fig. 49), developed by Detroit Edison Company for determining the film-

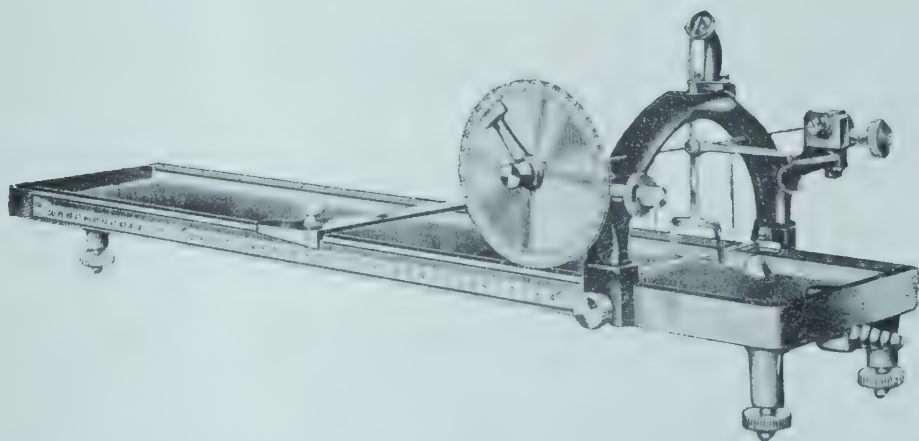


Fig. 49. Film or hydrophil balance. (Courtesy *Central Scientific Company*).

forming characteristics of oils, consists of a metal tray 65 cm. long, 14 cm. wide, and 1.5 cm. deep. A support which spans the tray carries a measuring device consisting of a torsion wire secured at both ends in torsion heads, each of which is driven by a worm gear arrangement which permits very precise adjustment.

The forward torsion head extends through a circular plate provided with a scale graduated from 0° to 360° and a vernier which permits readings to be made to 0.1° . This mechanism is attached to a mica float which rests lightly on the liquid medium. Any force exerted by the film on the mica float can be accurately measured by the torsion mechanism. The trough is graduated along its long dimension and is provided with a movable straight edge which permits changes to be made in the surface area of the film and makes possible the determination of any particular

area of the oily film that is formed by movement of the barrier. The film balance is applied in determining the force exerted against the float when the film is compressed to any corresponding area. The force is measured in dynes per centimeter and the area in square centimeters. Other types of film-pressure measuring devices have been described by Adam (12) as well as by others. They may be purchased from most apparatus supply houses.

Various methods may be used in producing the film to be investigated. A drop of liquid may be placed directly on the distilled water surface or the substance may be dissolved in a volatile solvent and the solution dropped on the water. On evaporation of the solvent, the film of the solute remains. In some cases a solid may be placed on the surface and allowed to spread. The long-chain fatty acids, higher alcohols, ethyl esters, glycerides, and natural oils have been extensively investigated with respect to their film-forming characteristics by means of various types of film balances.

Monomolecular Films of Saturated Fatty Acids on Distilled Water. Adam (13) made many qualitative measurements of the properties of monomolecular films including those formed by the even- and odd-numbered carbon acids from C_{12} to C_{26} . When spread on the surface of distilled water at a constant temperature of 20°C ., all of the saturated fatty acids were found to exhibit essentially similar behavior with respect to the compressibility of their films. This behavior is illustrated by the force-area curve reproduced (14) in Figure 50, from which it is seen that at areas greater than about 21×10^{-16} sq. cm. per molecule there is little or no measurable resistance to pressure. At this point there is observed a sudden opposition to further contraction, and the compressing force increases practically linearly with decreasing area up to the point at which the film collapses due to piling up of the molecules of the film.

These results may be interpreted as evidence that when the area of a film of saturated fatty acids has been reduced to the extent where the molecules are closely packed together, the area occupied per molecule is 21×10^{-16} sq. cm. and is independent of the length of the carbon chain. The fact that the molecules occupy the same area independent of the length of the carbon chain, and the fact that the area formed (21×10^{-16} sq. cm.) is the area of the cross section of a CH_2 group determined by other methods, is conclusive proof of the orientation of the molecules of fatty acids producing the film. It is evident, therefore, that because of the affinity of the hydrocarbon portion of the molecules for each other the molecules spread on the surface of the water only far enough for their

heads or hydrophilic parts to come in contact with water. The surface tension of the water, therefore, is not decreased unless enough fatty acid is added to cover the surface completely with a monomolecular film. By measuring the volume of fatty acid required to form a monomolecular film covering a given area, the thickness of the film can be calculated. Also, by placing a known number of molecules on the surface and measuring the area to which the film spreads before the surface tension becomes that of pure water, the area per molecule can be measured.

For comparison of the molecular areas of various compounds, the com-

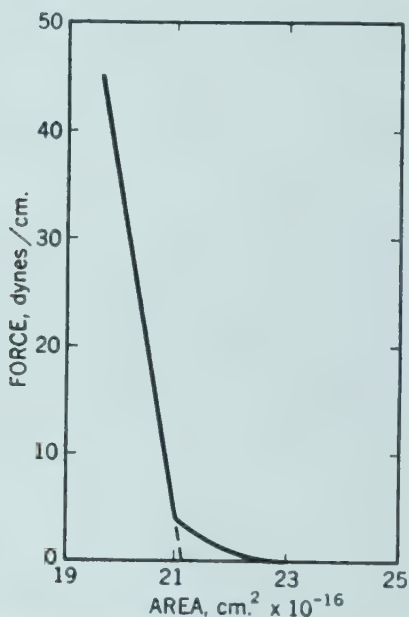


Fig. 50. Force-area curve for monomolecular films of saturated fatty acids on distilled water at 20°C. Data from H. S. Taylor (14).

pounds must be in the same physical state. Adam and Dyer (15) have shown that the molecular area per chain remains the same for one or for three chains per molecule, if both are in the same state.

There are many effects on monolayers caused by use of other than pure water as the substrate. The effect of ionization (16), monolayers of soap (17), decrease in area as alkalinity of substrate increases (18,19), etc., are some of these effects.

A mixture of fatty materials can give an increase in molecular area which is more than the sum of the individual components. Collet (20) found a maximum increase of 14% for a 1:1 mixture of trimyristin and

tripalmitin. Schulman and Hughes (21) found an increase in area with a mixture of oleic acid and cetyl alcohol.

Monomolecular Films of Saturated Fatty Acids on Dilute Acid Solutions. Adam (14) also measured the compressibility of the films formed with the saturated fatty acids on water at different pH values. When 0.01 *N* hydrochloric acid solutions were used, the force–area curves were found to differ from those obtained with pure distilled water, as may be seen by reference to Figure 51. With areas greater than about 25×10^{-16} sq. cm. per molecule, little or no resistance to compression is observed,

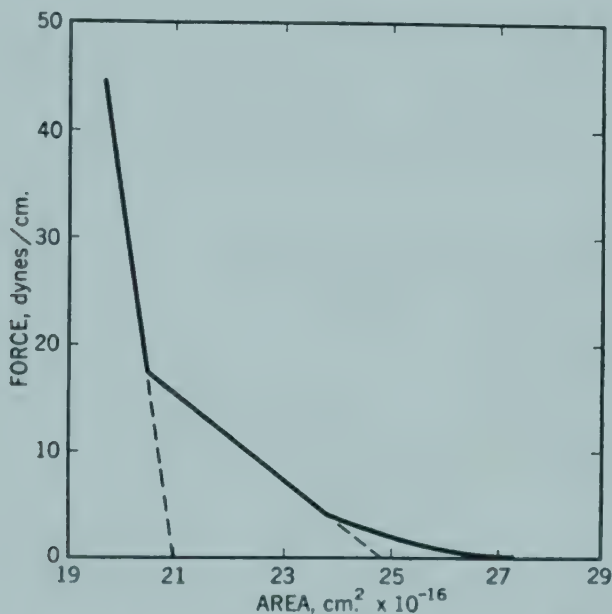


Fig. 51. Force–area curve for monomolecular films of saturated fatty acids on 0.01 *N* hydrochloric acid solution. Data from H. S. Taylor (14).

after which the compression force increases linearly to an area of 21×10^{-16} sq. cm. The slope of the curve changes sharply at this compression value and resembles that obtained with water up to the point where the film collapses.

This behavior of saturated fatty acid films is explained by the fact that the head of the molecule, i.e., the carboxyl group, occupies a greater area than the cross section of the chain. When the film is spread over distilled water, the cross section of the chain gives the effective area because of the different depths to which alternate molecules enter into the water. When the pH of the water is decreased, as in the case of 0.01

N hydrochloric acid solution, the attraction of the carboxyl group for the water decreases and forces all these groups to the same level.

The area, 25×10^{-16} sq. cm. per molecule, therefore, corresponds to the cross section of the polar (COOH) group, and the area, 21×10^{-16} sq. cm. per molecule, observed on compression to the point where the heads of the molecules have all been forced to the level at which all the carbon chains are again in close contact, corresponds to the cross section of the methylene (CH₂) group.

Dervichian investigated the spreading of stearic acid and trimyristin on *N*/1000 HCl (22); the Stenhagens, arachidonic on *N*/100 HCl (23). The molecular areas given are 23.5 Å.²

Effect of Temperature on Monomolecular Films. Another observation made by Adam relates to the effect of temperature on the compressibility of saturated fatty acid films. This effect is illustrated by the curve in Figure 52 for a monomolecular film of palmitic acid on 0.01 *N* hydro-

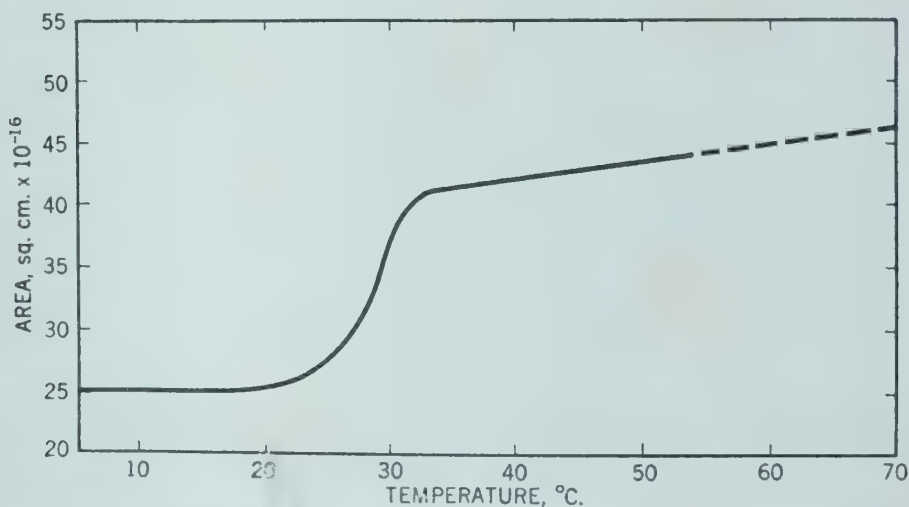


Fig. 52. Effect of temperature on compressibility of a monomolecular film of palmitic acid on 0.01 *N* hydrochloric acid under a constant force of 1.4 dynes per cm. Data from N. K. Adam (24).

chloric acid in which the temperature in °C. is plotted against the area in sq. cm. $\times 10^{-16}$ under a constant force of 1.4 dynes per cm. It may be seen from this figure that when the force is maintained at 1.4 dynes per cm. and the temperature is raised, the area remains constant at 25.1×10^{-16} sq. cm. per molecule from 0° to about 28°C. As the temperature is increased above 28° a sharp expansion of the area occurs which con-

tinues to about 35°C., after which the expansion likewise continues but at a very diminished rate. The expansion coefficient above 35°C. was found to correspond in magnitude to the thermal expansion coefficient of a gas and it was considered that a change in state occurred, analogous to the change of a solid to a gas.

It was found by Adam that, the longer the carbon chain, the higher was the observed temperature at which the expansion was observed (24). This change appears to be due to a separation of the molecules from one another at the surface, brought about by the thermal agitation becoming so violent that the lateral attractions of the molecules for each other are overcome. Films in this state are referred to as *expanded films* in contrast to *condensed films* where the molecules are in close contact at low temperatures. Expanded films may be described as being formed from close-packed condensed films by a rise in temperature, the change being complete in a few degrees at constant pressure, and being similar in nature irrespective of the substance.

Monomolecular Films of Other Long-Chain Acids. Adam and Jessop (25) examined the films formed by the dibasic acids containing 16, 20, 24, and 32 methylene groups, and the diethyl esters containing 10, 11, 16, 20, and 32 methylene groups and the monoethyl ester of octadecanedioic acid, $\text{COOH}(\text{CH}_2)_{16}\text{COOC}_2\text{H}_5$. All of the diethyl esters, $\text{C}_2\text{H}_5\text{OOC}(\text{CH})_n\text{COOC}_2\text{H}_5$, were observed to form monomolecular films. The dibasic acids formed similar films attached to the water surface by one carboxyl group only. The films were, however, rather unstable and tended to collapse under compression.

Adam also examined films formed on 0.01 *N* hydrochloric acid by a number of unsaturated acids, including 2-octadecenoic, 9-octadecenoic (oleic), elaidic, erucic, and brassidic acids. All of these acids produced films in the expanded state. The presence of double bonds in the middle of the chain caused the films to expand more easily than films with saturated chains of similar length. Since unsaturated hydrocarbons behave similarly, it is assumed that the double bond attracts water more than a saturated linkage. *Cis*- and *trans*-acids behave somewhat differently. The *cis*-form is more strongly attracted to the water than the *trans*-form. A double bond near the carboxyl group, as in 2-octadecenoic acid, lowers the expansion of the film compared with that observed when the double bond is near the middle of the chain.

By means of a Langmuir film balance, Krum and Muller (25a) determined that monolayer films of oleic acid on water become multilayer on compression, and return to monolayers on expansion. High polymers, in-

cluding poly(vinyl acetate), poly(vinyl ether), acrylic acid ethyl ester, and stearic acid also show complete reversibility.

The molecular areas of other aliphatic compounds have been determined by various investigators. A series of branched-chain palmitic and stearic acids were found by Weitzel *et al.* (26) to have molecular areas which varied with the position of the branching methyl group as determined by a shear method (26a). Stenhagen (27) investigated the disubstituted acetic acids, and found their molecular areas to be 55–56 A.², which values are consistent with those (27–29 A.²) for the area per chain of the normal acid and its triglyceride. See also 27a, 27b, 27c.

Monolayers of ω -branched fatty acids containing 16 to 24 carbon atoms, and the alkyl esters of palmitic acid with 1 to 16 carbon atoms in the alkyl chain, were investigated by Sobotka *et al.* (28) and Adam (29), respectively. However, changes of state precluded definite determination of their molecular areas.

Fatty acids and glycerides having two or more double bonds exhibit interesting behaviors. If the double bonds are remote from the carboxyl end group, expanded films are formed in which the limiting area increases with the number of double bonds in the molecule. Stearolic acid with a triple bond, eleostearic acid with three conjugated double bonds, triricinolein containing three double bonds and three hydroxyl groups, exhibit characteristic film-forming properties. Many other lipids, including sterols, phosphatides, ketones, alcohols, amides, nitriles, etc., have been examined with respect to their film-forming properties.

TABLE 160
Molecular Dimensions of Long-Chain Aliphatic Acids and Related
Compounds Calculated from Monomolecular Film Measurements

Substance	Number of carbon atoms	Head group	Cross sections, A. (as packed in films)		Approx. length, A.
			Chain	Head	
Myristic acid	14	—CH ₂ —CH ₂ —COOH	21.0	25.1	21.1
Pentadecanoic acid	15	—CH ₂ —CH ₂ —COOH	21.0	25.1	22.4
Stearic acid	18	—CH ₂ —CH ₂ —COOH	21.0	25.1	26.2
Behenic acid	22	—CH ₂ —CH ₂ —COOH	21.0	25.1	31.4
Iso-oleic acid	18	—CH=CH—COOH	21.0	28.7	26.2
Octadecyl urea	19	—NH—CO—NH ₂	21.0	26.3	28.8
Stearic amide	18	—CONH ₂	21.0	>21.5	26.1
Ethyl palmitate	18	—COOC ₂ H ₅	21.0	22.3	26.1
Ethyl behenate	24	—COOC ₂ H ₅	21.0	22.3	34.0
Cetyl alcohol	16	—CH ₂ OH	21.0	21.7	22.4
Stearic nitrile	18	—CH ₂ CN	21.0	27.5	

The data obtained by measurement of the properties of the monomolecular films of the long-chain fatty acids and related compounds have been used for calculating certain molecular dimensions of these compounds, e.g., cross-section areas, chain length, etc., as shown in Table 160. The values thus obtained are generally smaller than those obtained by x-ray measurement, which would indicate these compounds are more closely packed in monomolecular films than in crystals and are comparable with the actual dimensions of the molecule.

For a more detailed treatment of the above-mentioned work on monomolecular films, the reader is referred to general work of Adam (34) on surface films and to the thermodynamic treatment by Harkins (35) of film formation and the effect of compression on surface films of fatty acids, alcohols, and esters.

TABLE 161
Force-Area and Related Data from Monomolecular Film
Measurements of Linseed Oil Acids and Esters (36)

Compound	Refractive index	Mol. wt.	Area, $\text{cm.}^2 \times 10^{-16}$ cm.	Molecule length, cm. $\times 10^{-8}$	Area per mol. at point of collapse, $\text{cm.}^2 \times 10^{-16}$	Force at point of collapse, dynes/cm.
Stearic acid		284.3	22.5	21.9	18	60
Oleic acid	1.4606	282.3	52	10.2	28	28
Mixed acids ^a	1.4728	280	67	8.2	28	28
Oleic monoglyceride	1.4605	356	47	12.8	25	29
Oleic diglyceride	1.4661	621	86	12.7	63	16.7
Oleic triglyceride	1.4709	885	127	12.3	100	12.3
Stearic monoglyceride		358	27	20.6	20	55
Stearic diglyceride		625	49	21.3	41	56
Stearic triglyceride		891	72	21.5		
Mixed monoglyceride	1.4788	354	61	10.3	35	25
Mixed diglyceride	1.4811	617	103	10.3	73	15
Mixed triglyceride	1.4832	879	143	10.7	110	12
Lead oleate		767	100	10.5	47	27
Manganese linoleate		615	125	7.46	57	26.5
Ethylene glycol ester ^a	1.4779	586	98	10.9	72	14
Dimannitol ester ^a	1.4880	706	105	11.5	75	15
Diethylene glycol ester ^a	1.4777	630	110	10.2	73	18.4
Tetramannitol ester ^a	1.4880	1230	176	12.1	147	8.2

^a Chilled, filtered, and distilled fatty acids of linseed oil.

Monomolecular Films of Glycerides. Long *et al.* (36) applied a modified Langmuir film balance in measuring the force-area values of monomolecular films of stearic and oleic acids and the corresponding mono-, di-, and triglycerides as well as a number of other esters and salts, with the results shown in Table 161.

The molecular structures in the monolayers of saturated isomeric 1- and 2-monoglycerides were investigated by Merker and Daubert (36a), who concluded that the orientation of the molecules in the condensed monolayers approximated the orientation in the anhydrous three-dimensional crystals. They also determined the densities of the pure liquids with pycnometers and extrapolated linearly to 20.0°C. and to the melting points of the monoglycerides. The results are given in Table 161a.

TABLE 161a
Densities and Molecular Dimensions of Monoglycerides (36a)

Material	Solid state				Hypothetical liquid state			
	Density, g./ml. 21°C.	Cross-sectional area, Å ²		M.p. °C.	Extrapolated density, g./ml. m.p. 20°C		Cross-sectional area, Å ² , 20°	
		Tilt, 59°	⊥ to chain				Tilt, 59°	⊥ to chain
1-Monocaprin	1.090	23.0	19.7	52.8	0.976	0.999	25.1	21.5
1-Monolaurin	1.080	22.9	19.6	63.0	0.952	0.982	25.1	21.5
1-Monomyrustin	1.071	22.6	19.4	70.2	0.933	0.969	25.0	21.4
1-Monopalmitin	1.064	22.6	19.4	76.8	0.919	0.959	25.0	21.4
1-Monostearin	1.057	22.5	19.3	80.5	0.906	0.948	25.1	21.5
		Tilt, 45°					Tilt, 45°	
2-Monocaprin	1.087	25.6	18.1	40.4	0.984	0.998	27.9	19.7
2-Monomyrustin	1.068	26.0	18.4	61.2	0.942	0.972	28.5	20.2
2-Monopalmitin	1.062	25.8	18.2	68.9	0.926	0.960	28.5	20.2
2-Monostearin	1.059	25.7	18.2	74.4	0.918	0.955	28.5	20.2

The cross-section area of stearic acid found by Adam, Langmuir, and Long *et al.* from monomolecular film measurements are in good agreement with one another, namely, 21.0, 22.0, and 22.5 cm.² × 10⁻¹⁶. Comparative values for oleic acid, triolein, and tristearin found by Langmuir and by Long *et al.* are 52 and 52, 126 and 127, and 66 and 72 cm.² × 10⁻¹⁶, respectively.

Long *et al.* (36) also examined films produced with a number of oxidized and bodied linseed oils, and found that oxidation and heat bodying

resulted in appreciable change in the force-area of these oils compared with untreated oils. The changes in area and in the shape of the force-area curves were found to be a function of the time and temperature of "blowing," as indicated in Figure 53. The changes in these curves were found to be of sufficient magnitude to permit the use of the method as a means of following variations occurring during heat bodying of linseed oil.

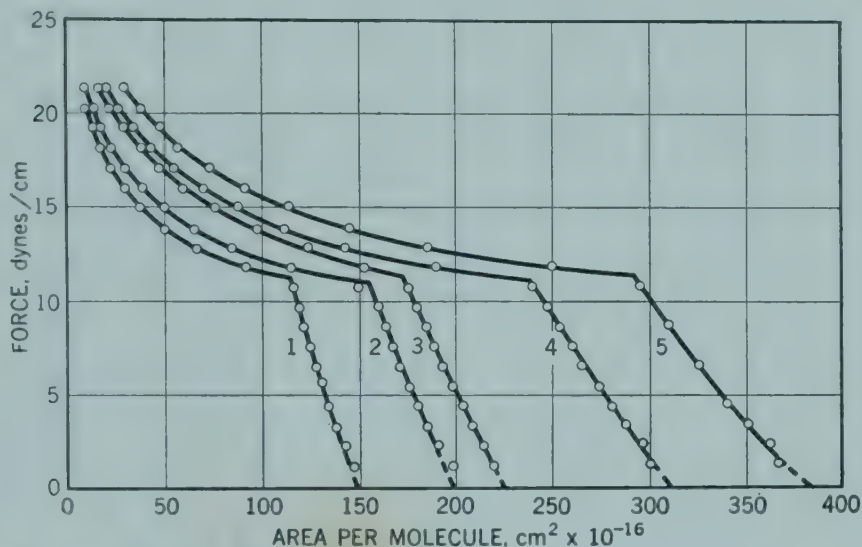


Fig. 53. Effect of heat bodying at 293°C. on the force-area curves of monomolecular films of refrigerated linseed oil with 0.028% cobalt as linoleate (36). Curve 1: 0.75 testing hr., 960 mol. wgt.; curve 2: 2.25 testing hrs., 1332 mol. wgt.; curve 3: 3.00 testing hrs., 1510 mol. wgt.; curve 4: 4.50 testing hrs., 2223 mol. wgt.; curve 5: 5.50 testing hrs., 2500 mol. wgt.

Effect of Pressure on Monomolecular Films. At the triple point, the molecular area per chain is ca. 38–38 Å.² for fatty acids, and ca. 115–120 Å.² for triglycerides. Under isothermal conditions, fatty substances undergo different types of phase changes as the surface pressure on monomolecular films is varied. The monolayer of tricaproin, for example, is comparable to a gas in that it can be compressed to a small volume without a phase change, as reported by Dervichian (37). Other materials may go through one or two phase changes under increasing pressure.

Those fatty acids and esters for which molecular film data have been reported can be classified into two groups, in one of which the cross-section area per chain is 27–29 Å.² and in which the monolayer is fluid. Included in this group are myristic acid at 34°C. (25), triolein at room

temperature (22), trimyristin at 44°C. (22), and pentadecylic acid above 35°C. (38).

In the second group, in which the cross-section area per chain is 27–39 Å.² in the first phase transformation and ca. 19.5 Å.² at the second transformation, is myristic acid at 12°C. (25) and 21°C. (22), trilaurin at 14°C. (22), and pentadecylic acid at 20°C. (38).

Ethyl palmitate at 15°C. exhibits no discontinuity (25).

(b) Polymolecular Films

In contrast to monomolecular films formed by long-chain fatty acids and their derivatives on the surface of water, polymolecular films can be built up on metals by the Langmuir-Blodgett (39) method. These polymolecular films, or layers of molecules, are formed by transferring any number of monomolecular films to a metallic block having a highly polished surface or to foils of transparent Resoglaz, by dipping them through a monomolecular film on a water surface. By minor variations in the technique of preparation it is possible to deposit either an even or an odd number of monolayers to produce a polylayer of any desired thickness, or to deposit layers of different polymorphic forms of the same substance.

Polymolecular films thus formed can be examined by means of electron diffraction, using reflection methods if produced on metals and transmission methods if produced on transparent Resoglaz. When a beam of electrons is permitted to fall on deposited films of these types, the electrons are diffracted like light waves and the diffraction pattern thus produced can be recorded on a photographic plate just as in the case of x-ray diffraction. Analysis of the diffraction pattern thus produced makes possible the determination of the arrangement of the molecules forming the multimolecular layer (40).

Germer and Storks (41) examined, by means of electron diffraction patterns, various long-chain fatty acids and their barium soaps using both reflection and transmission methods. They found that the hydrocarbon chains of barium stearate molecules formed hexagonal arrays with their axes normal to the supporting surface and separated by distances of 4.85 Å. Stearic acid molecules formed monoclinic crystals having the dimensions $a = 8.27$ Å., $b = 4.96$ Å., $\beta = 70^\circ$, the a and b axes lying in the plane of the supporting surface. These dimensions are somewhat greater than those obtained by Müller (42) from x-ray measurements of the crystal, which are: $a = 5.54$ Å., $b = 7.38$ Å., $\beta = 63^\circ 38'$.

Stenhagen (43) prepared and examined a large number of built-up films of fatty acid monoesters and di- and triglycerides. He found that the

molecules in these films in the crystal state can be arranged in four different ways i.e., the lattice planes can be separated by one or two, inclined, or vertically oriented molecules. Built-up films of fatty acids and their barium, calcium, magnesium, copper, and lead salts have been examined by x-ray (44-47) and by electron diffraction methods (48).

4. Nonaqueous Solutions

(a) Solubility at Ordinary and Elevated Temperatures

The solubility behavior of the fatty acids, especially the higher fatty acids, and their derivatives in organic solvents is of considerable theoretical and industrial importance. Solubility data for the lowest members of the series in a wide variety of organic solvents are available and complete phase diagrams for many of these systems have been constructed. Numerous investigations dealing with systems composed of one or more of the first six members (formic to caproic) of the fatty acids series and various organic solvents have been reported and the data therefrom have been compiled by Seidell (6).

Data with respect to the solubilities of the organic solvent-fatty acid systems from caprylic to stearic acid at moderate temperatures are due almost entirely to the efforts of Ralston and co-workers (4,49). These investigators determined the solubilities of eleven fatty acids in fifteen different organic solvents, including hydrocarbons, chlorinated hydrocarbons, alcohols, ketones, glacial acetic acid, esters, and nitrogen-containing solvents (30,31). Owing to the wide utility of these data, they are reproduced in tabular form in Tables 162 to 176, and, in the case of eleven of the solvents, in graphic form in Figures 54 to 64. The numbers in the tables and on the curves refer to the total number of carbon atoms in each acid investigated. The acids used in the solubility determinations were of relatively high purity judged by their freezing points. The solubilities were generally measured either from 0°C. or from the freezing point of the solution to 100°C. in the case of solvents boiling above this temperature.

Two striking phenomena may be noted in the results of the work of Ralston *et al.* (4,49) on the organic solvent-fatty acid systems, namely, the tendency toward pairing of the solubility curves and the formation of eutectics between some of the solvents and fatty acids. Eutectic formation with benzene, cyclohexane, and acetic acid was observed in the case of all the acids investigated. The composition of these eutectics and the corresponding eutectic temperatures have been assembled in Table 177.

TABLE 162
Solubilities of Fatty Acids in Benzene (7)

Number of C atoms	Grams acid per 100 g. benzene					
	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	770	∞	∞	∞	∞	∞
9	2680	∞	∞	∞	∞	∞
10	145	398	8230	∞	∞	∞
11	208	663	∞	∞	∞	∞
12	32.3	93.6	260	1390	∞	∞
13	42.4	117	354	7600	∞	∞
14	6.95	29.2	87.4	239	1290	∞
15	8.84	36.2	103	295	2280	∞
16	1.04	7.30	34.8	105	306	2170
17	1.52	9.23	42.1	121	369	5450
18	0.24	2.46	12.4	51.0	145	468

TABLE 163
Solubilities of Fatty Acids in Cyclohexane (4)

Number of C atoms	Grams acid per 100 g. cyclohexane					
	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	670	∞	∞	∞	∞	∞
9	2340	∞	∞	∞	∞	∞
10	103	342	7600	∞	∞	∞
11	150	525	∞	∞	∞	∞
12	19.8	68	215	1310	∞	∞
13	31.0	100	330	8200	∞	∞
14	5.3	21.5	72	217	1310	∞
15	6.8	27.1	88	277	2460	∞
16	0.9	6.5	27.4	92	285	2530
17	1.5	8.4	34.0	108	365	7600
18	0.2	2.4	10.5	43.8	133	450

TABLE 164
Solubilities of Fatty Acids in Trichloromethane (4)

Number of C atoms	Grams acid per 100 g. trichloromethane						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	213	720	∞	∞	∞	∞	∞
9	336	2340	∞	∞	∞	∞	∞
10	61	122	326	6550	∞	∞	∞
11	74	161	485	∞	∞	∞	∞
12	22.4	39.1	83	207	2120	∞	∞
13	28.4	53	116	315	6550	∞	∞
14	8.1	15.1	32.5	78	205	1000	∞
15	9.5	17.7	38.1	91	246	1750	∞
16	2.9	6.0	15.1	36.4	91	250	1820
17	3.6	7.5	17.8	42.6	106	297	5000
18	0.4	2.0	6.0	17.5	48.7	124	365

TABLE 165
Solubilities of Fatty Acids in Tetrachloromethane (4)

Number of C atoms	Grams acid per 100 g. tetrachloromethane						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	115	370	∞	∞	∞	∞	∞
9	158	1150	∞	∞	∞	∞	∞
10	27.0	64	210	4650	∞	∞	∞
11	35.1	88	318	∞	∞	∞	∞
12	9.2	20.5	53	160	835	∞	∞
13	11.2	26.9	75	240	5450	∞	∞
14	3.2	6.8	17.6	55	166	870	∞
15	3.8	8.4	22.2	69	208	1560	∞
16	0.6	1.8	5.8	21.5	72	212	1590
17	0.7	2.0	6.8	25.1	83	250	4650
18		0.2	2.4	10.7	36.4	108	325

TABLE 166
Solubilities of Fatty Acids in Methanol (4)

Number of C atoms	Grams acid per 100 g. methanol						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	330	1300	∞	∞	∞	∞	∞
9	510	4650	∞	∞	∞	∞	∞
10	80	180	510	9900	∞	∞	∞
11	105	235	740	∞	∞	∞	∞
12	12.7	41.1	120	383	2250	∞	∞
13	12.6	48.5	148	515	14000	∞	∞
14	2.8	5.8	17.3	75	350	2670	∞
15	2.2	5.0	16.4	75	400	4400	∞
16	0.8	1.3	3.7	13.4	77	420	4650
17	0.1	0.7	2.5	9.9	62	500	12000
18			0.1	1.8	11.7	78	520

TABLE 167
Solubilities of Fatty Acids in Ethanol (7)

Ethanol, % by wt.	Number of C atoms	Grams acid per 100 g. ethanol						
		0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
99.4	12	20.4	41.6	105	292	1540	∞	∞
	14	7.07	9.77	23.9	84.7	263	1560	∞
	16	1.89	3.20	7.21	23.9	94.2	320	2600
	17	2.04	2.98	6.62	22.2	110	388	8230
	18	0.42	1.09	2.25	5.43	22.7	105	400
95.0	8	262	1035	∞	∞	∞	∞	∞
	9	393	3230	∞	∞	∞	∞	∞
	10	60.6	93.5	440	8980	∞	∞	∞
	11	85.2	190	706	∞	∞	∞	∞
	12	15.2	34.0	91.2	260	1410	∞	∞
	13	15.5	34.5	104	336	6560	∞	∞
	14	3.86	7.64	18.9	68.7	238	1485	∞
	15	3.82	7.18	19.5	78.5	295	2460	∞
	16	0.85	2.10	4.93	16.7	73.4	287	2280
	17	1.03	1.68	4.17	15.3	84.2	344	6560
	18	0.24	0.65	1.13	3.42	17.1	83.9	365
91.1	16	0.76	1.94	4.60	15.3			
	18	0.13	0.35	0.66	2.30	13.5	68.7	
80.8	18	ca. 0.06	0.10	0.20	0.81	3.20	50.8	238

TABLE 168
Solubilities of Fatty Acids in Isopropanol (4)

Number of C atoms	Grams acid per 100 g. isopropanol						
	0.0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	280	900	∞	∞	∞	∞	∞
9	422	2920	∞	∞	∞	∞	∞
10	67	140	360	5750	∞	∞	∞
11	82	182	540	∞	∞	∞	∞
12	21.5	44.1	100	253	1270	∞	∞
13	22.1	52	125	340	6550	∞	∞
14	7.2	13.6	31.6	82	230	1210	∞
15	6.2	13.3	34.4	95	282	2070	∞
16	2.4	4.6	10.9	32.3	94	270	2460
17	1.2	3.0	10.8	37.9	108	345	6550
18	≈0.1	0.4	2.0	10.0	38.1	118	422

TABLE 169
Solubilities of Fatty Acids in *n*-Butanol (4)

Number of C atoms	Grams acid per 100 g. <i>n</i> -butanol						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	225	750	∞	∞	∞	∞	∞
9	355	2530	∞	∞	∞	∞	∞
10	59	103	280	4650	∞	∞	∞
11	64	131	415	∞	∞	∞	∞
12	21.4	37.2	83	217	1070	∞	∞
13	21.5	39.8	100	295	5750	∞	∞
14	7.3	13.1	28.7	71	194	980	∞
15	7.1	12.5	28.4	74	220	1680	∞
16	1.9	4.2	10.5	30.0	84	243	1960
17	1.6	3.6	9.5	27.4	85	274	4900
18		0.2	1.6	9.0	36.2	111	370

TABLE 170
Solubilities of Fatty Acids in Acetone (7)

Number of C atoms	Grams acid per 100 g. acetone					
	0°C.	10°C.	20°C.	30°C.	40°C.	56.5°C.
8	221	975	∞	∞	∞	∞
9	356	3740	∞	∞	∞	∞
10	45.3	112	407	4660	∞	∞
11	50.2	149	706	∞	∞	∞
12	8.95	21.9	60.5	218	1590	∞
13	7.52	20.2	78.6	316	8230	∞
14	2.75	6.50	15.9	42.5	149	∞
15	2.20	5.27	13.8	49.3	183	∞
16	0.60	1.94	5.38	15.6	58.0	880
17	0.40	1.50	4.28	14.6	67.5	1330
18	0.21	0.80	1.54	4.93	17.0	220

TABLE 171
Solubilities of Fatty Acids in 2-Butanone (7)

Number of C atoms	Grams acid per 100 g. 2-butanone						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
10	42.4	100	318	7040	∞	∞	∞
11	47.9	139	521	∞	∞	∞	∞
12	11.5	24.7	64.7	202	1825	∞	∞
13	11.9	29.5	95.0	315	8230	∞	∞
14	4.28	8.46	18.5	54.3	189	1230	∞
15	4.28	8.70	20.2	70.4	257	2530	∞
16	0.90	3.09	8.57	20.6	66.1	228	2390
17	0.71	2.88	7.41	20.3	77.7	288	6560
18	0.25	1.01	2.99	8.34	24.8	84.7	344

TABLE 172
Solubilities of Fatty Acids in Glacial Acetic Acid (7)

Number of C atoms	Grams acid per 100 g. glacial acetic acid				
	20°C.	30°C.	40°C.	50°C.	60°C.
10	567	8230	∞	∞	∞
11	800	∞	∞	∞	∞
12	81.8	297	1480	∞	∞
13	96.8	395	8230	∞	∞
14	10.2	51.1	289	1410	∞
15	8.76	62.0	350	2600	∞
16	2.14	8.11	51.7	313	2280
17	1.27	6.52	61.0	384	6560
18	0.12	1.68	7.58	74.8	485

TABLE 173
Solubilities of Fatty Acids in Ethyl Acetate (4)

Number of C atoms	Grams acid per 100 g. ethyl acetate						
	0°C.	10°C.	-20°C.	30°C.	40°C.	50°C.	60°C.
8	161	610	∞	∞	∞	∞	∞
9	250	2020	∞	∞	∞	∞	∞
10	34.2	90	289	7850	∞	∞	∞
11	38.7	114	425	∞	∞	∞	∞
12	9.4	18.5	52	250	1250	∞	∞
13	10.1	22.5	70	281	8200	∞	∞
14	3.4	6.6	15.3	44.7	164	1350	∞
15	2.8	6.2	15.4	51	208	2370	∞
16	0.8	2.2	6.1	17.6	53	203	2340
17	0.4	1.6	5.3	16.8	59	242	6000
18			0.5	5.2	21.6	78	348

TABLE 174
Solubilities of Fatty Acids in Butyl Acetate (4)

Number of C atoms	Grams acid per 100 g. butyl acetate						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	206	700	∞	∞	∞	∞	∞
9	316	2340	∞	∞	∞	∞	∞
10	44.6	111	330	8230	∞	∞	∞
11	55	145	515	∞	∞	∞	∞
12	13.0	26.8	68	212	1350	∞	∞
13	14.5	33.0	95	322	9000	∞	∞
14	4.8	9.9	21.6	61	208	1370	∞
15	4.5	9.7	22.3	66	253	2460	∞
16	1.5	3.8	8.9	23.4	69	226	2330
17	1.2	3.5	8.7	24.0	75	269	6350
18	<0.1	0.2	1.6	8.1	28.7	97	350

TABLE 175
Solubilities of Fatty Acids in Nitroethane (4)

Number of C atoms	Grams acid per 100 g. nitroethane						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	25.2	790	∞	∞	∞	∞	∞
9	45.0	2340	∞	∞	∞	∞	∞
10	9.2	12.5	55	7000	∞	∞	∞
11	8.1	13.2	131	∞	∞	∞	∞
12	1.9	2.8	5.4	16.3	1460	∞	∞
13	1.4	2.1	4.5	17.3	9000	∞	∞
14	0.3	0.5	1.2	3.3	10.7	1180	∞
15	0.1	0.2	0.7	2.4	10.2	2460	∞
16			<0.1	0.7	2.6	10.0	1650
17				0.2	1.9	9.6	4250
18					0.3	2.7	14.0

TABLE 176
Solubilities of Fatty Acids in Acetonitrile (4)

Number of C atoms	Grams acid per 100 g. acetonitrile						
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
8	44.5	1020	∞	∞	∞	∞	∞
9	51	3470	∞	∞	∞	∞	∞
10	11.8	21.0	66	7600	∞	∞	∞
11	8.7	17.3	185	∞	∞	∞	∞
12	2.1	2.8	7.6	24.4	1540	∞	∞
13	1.4	2.0	5.8	21.4	8600	∞	∞
14	0.7	0.9	1.8	4.1	13.0	1210	∞
15	0.4	0.5	1.1	2.9	10.5	2460	∞
16	<0.1	0.2	0.4	1.0	2.8	9.9	1200
17		<0.1	0.2	0.6	1.9	8.3	3600
18			<0.1	0.3	0.8	2.0	10.3

TABLE 177
Eutectic Compositions of Saturated Fatty Acids
with Various Organic Solvents

Acid	Eutectic with benzene		Eutectic with cyclohexane		Eutectic with acetic acid	
	Fatty acid, % by wt.	Temp., °C.	Fatty acid % by wt.	Temp., °C.	Fatty acid, % by wt.	Temp., °C.
Caproic					97.7	-5.4
Heptanoic					98.8	-6.5
Caprylic	50.4	-10.5	22.0	-14.0	80.0	3.1
Nonanoic	54.0	-13.1	23.9	-17.5	83.6	1.6
Capric	34.5	-2.0	14.1	-3.2	55.1	8.6
Undecanoic	38.9	-4.0	16.2	-5.9	57.5	8.0
Lauric	11.2	4.5	6.8	3.2	17.3	12.8
Tridecanoic	14.6	3.7	8.6	1.9	15.9	13.1
Myristic	2.88	5.20	2.4	5.6	5.3	15.18
Pentadecanoic	3.65	5.15	2.9	5.4	4.3	15.40
Palmitic	0.19	5.40	0.4	6.4	1.23	16.17
Heptadecanoic	0.42	5.35	0.7	6.3	0.58	16.34
Stearic	0.015	5.50	<0.1	≈6.6	0.03	16.48

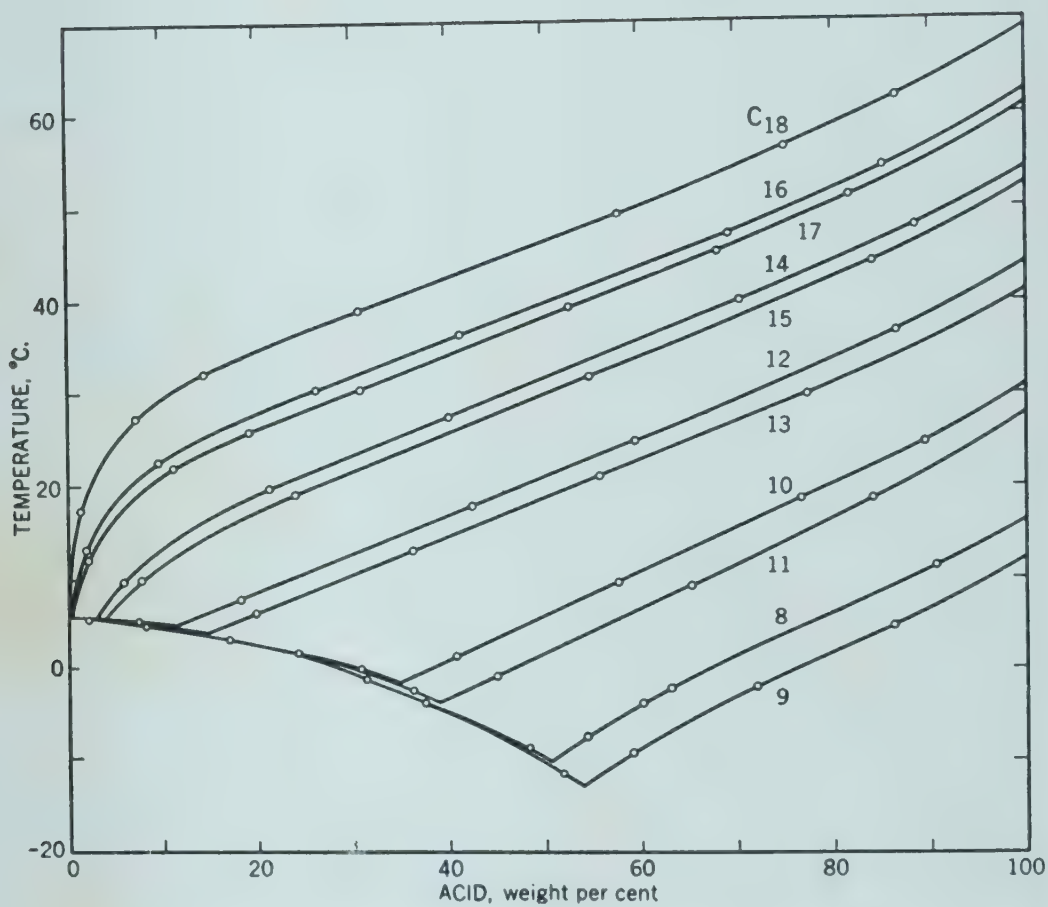


Fig. 54. Solubilities of fatty acids in anhydrous benzene (7).

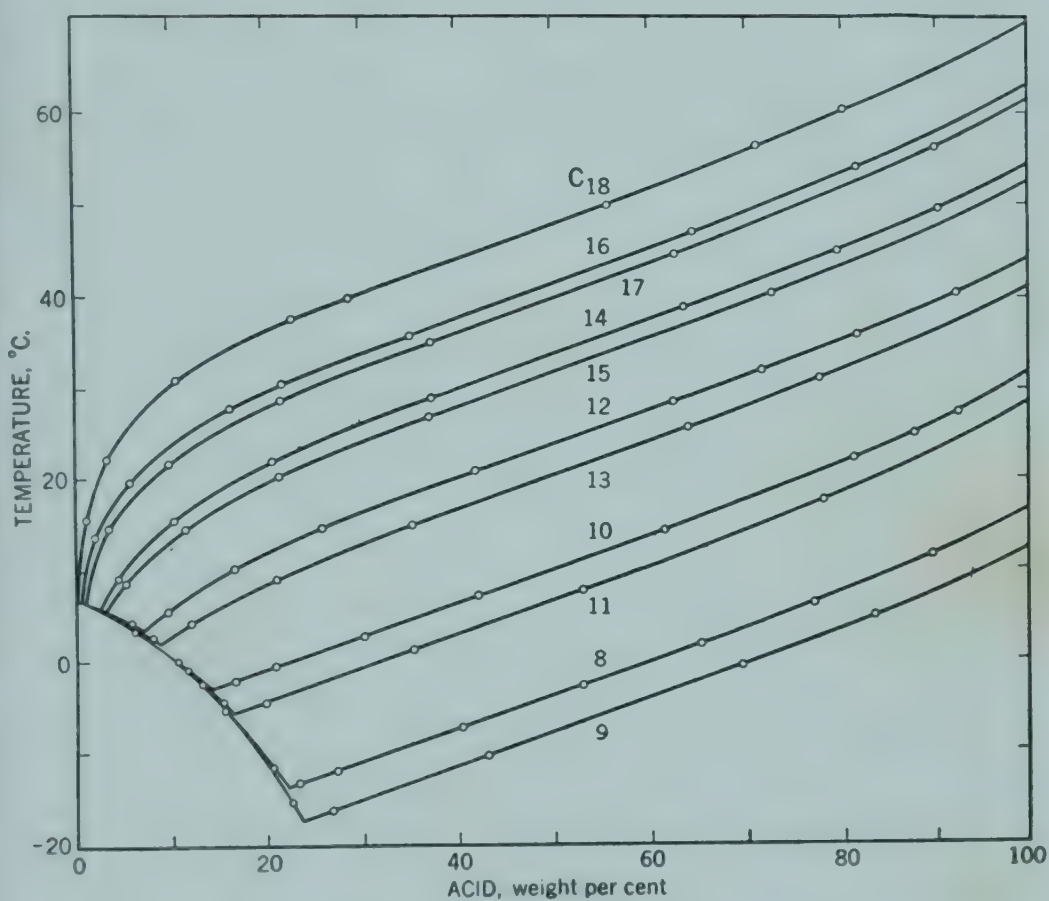


Fig. 55. Solubilities of fatty acids in cyclohexane (49).

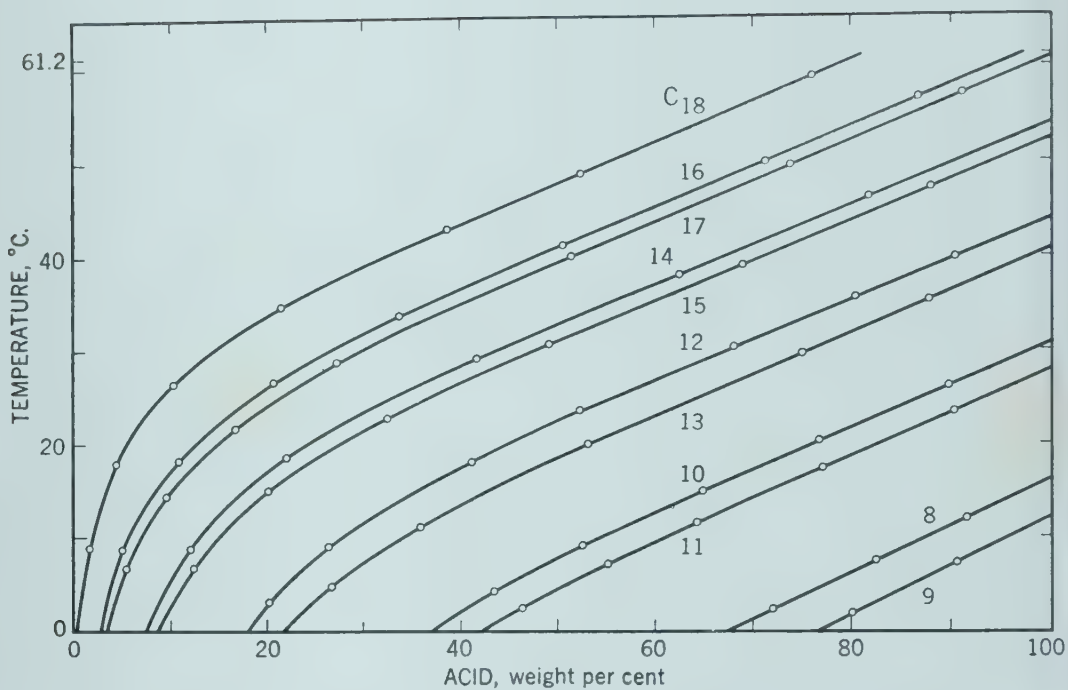


Fig. 56. Solubilities of fatty acids in trichloromethane (49).

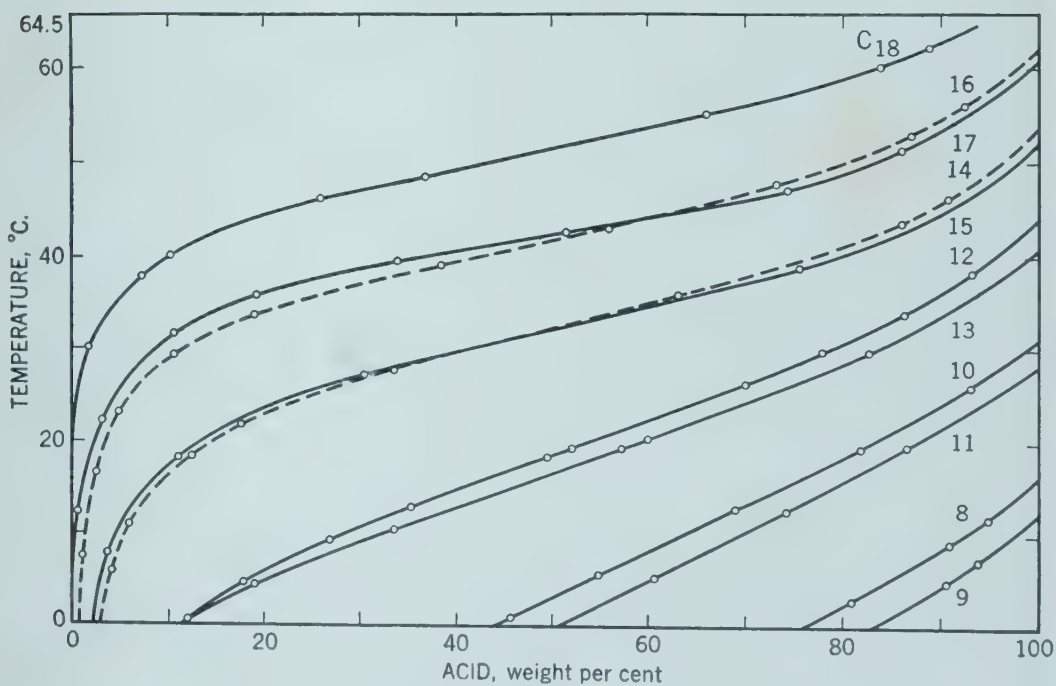


Fig. 57. Solubilities of fatty acids in methanol (49).

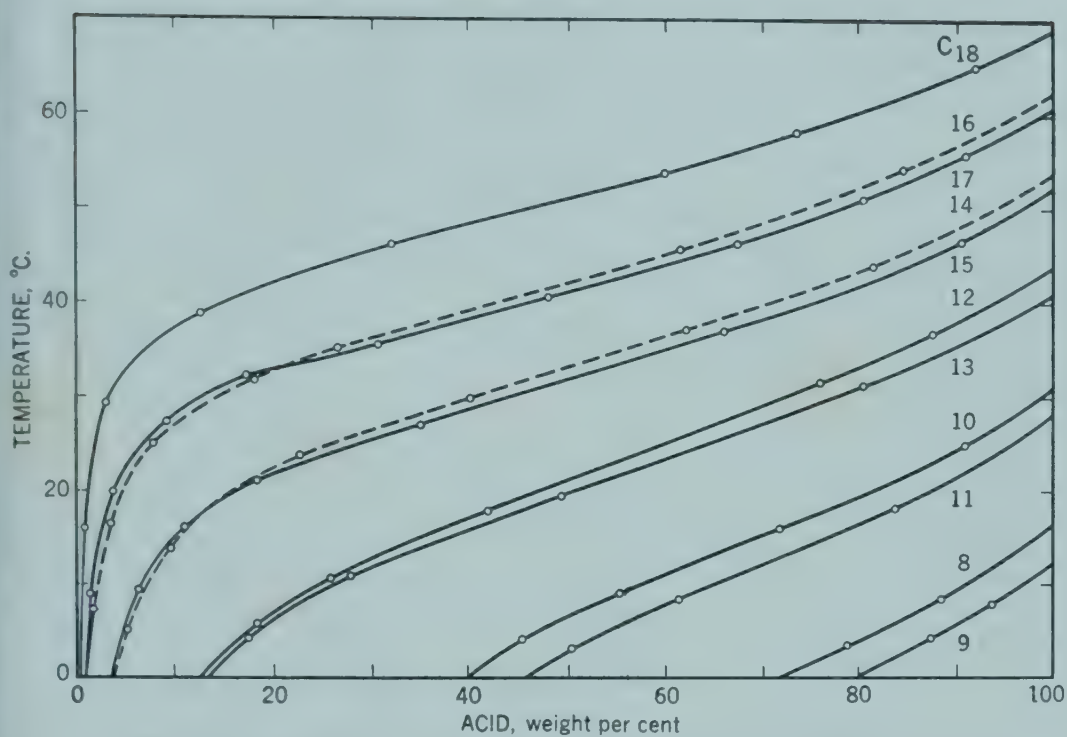
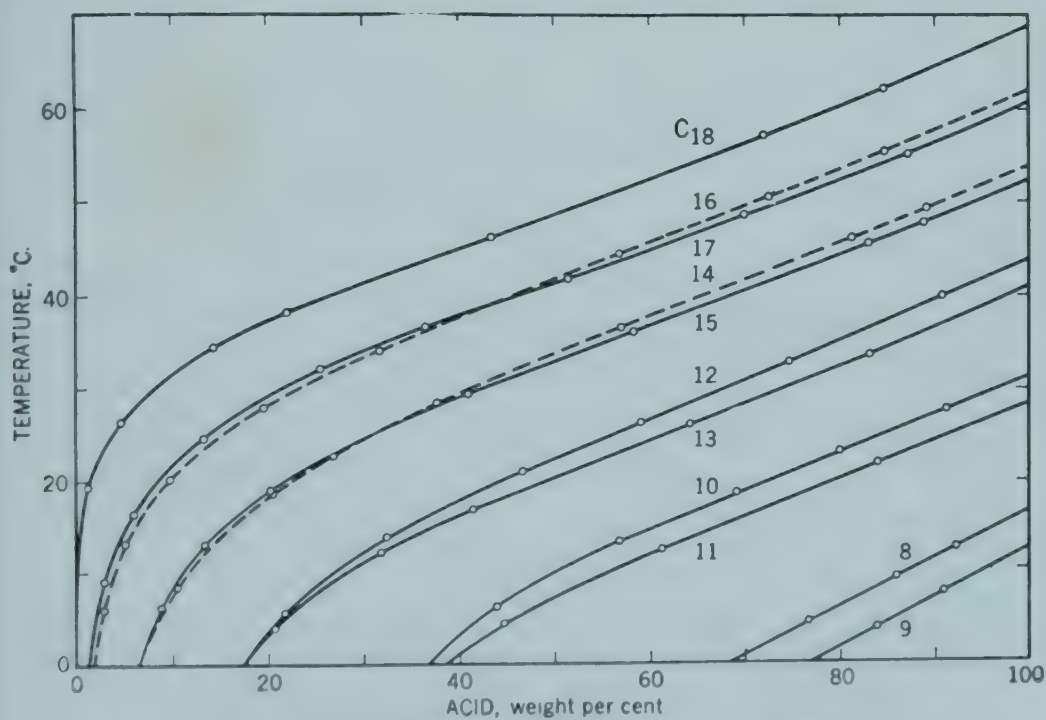


Fig. 58. Solubilities of fatty acids in ethanol (95% by weight) (7).

Fig. 59. Solubilities of fatty acids in *n*-butanol (49).

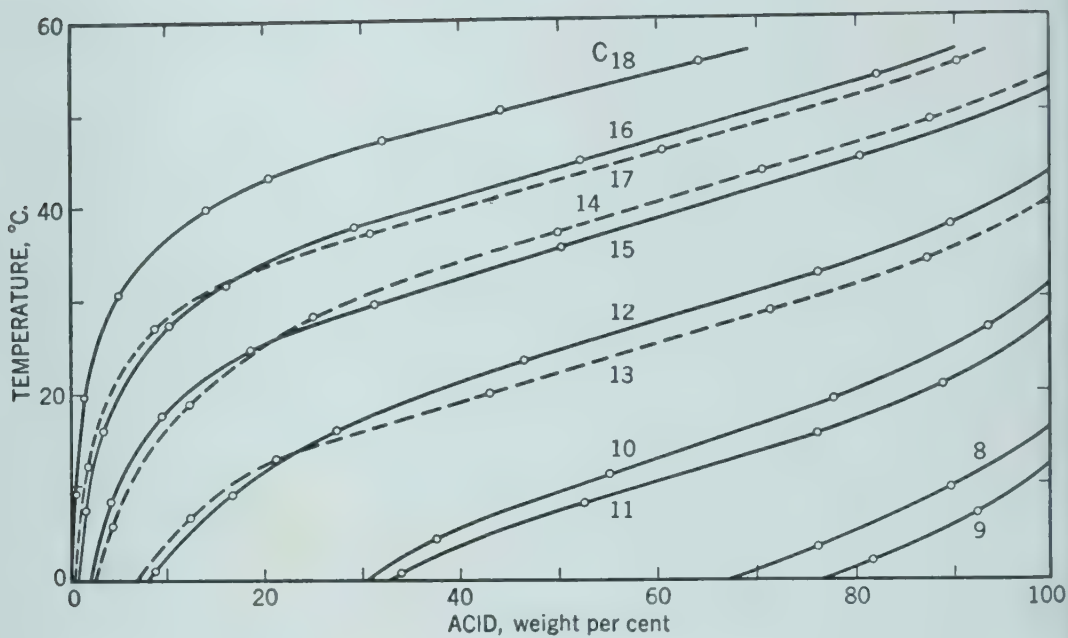


Fig. 60. Solubilities of fatty acids in acetone (7).

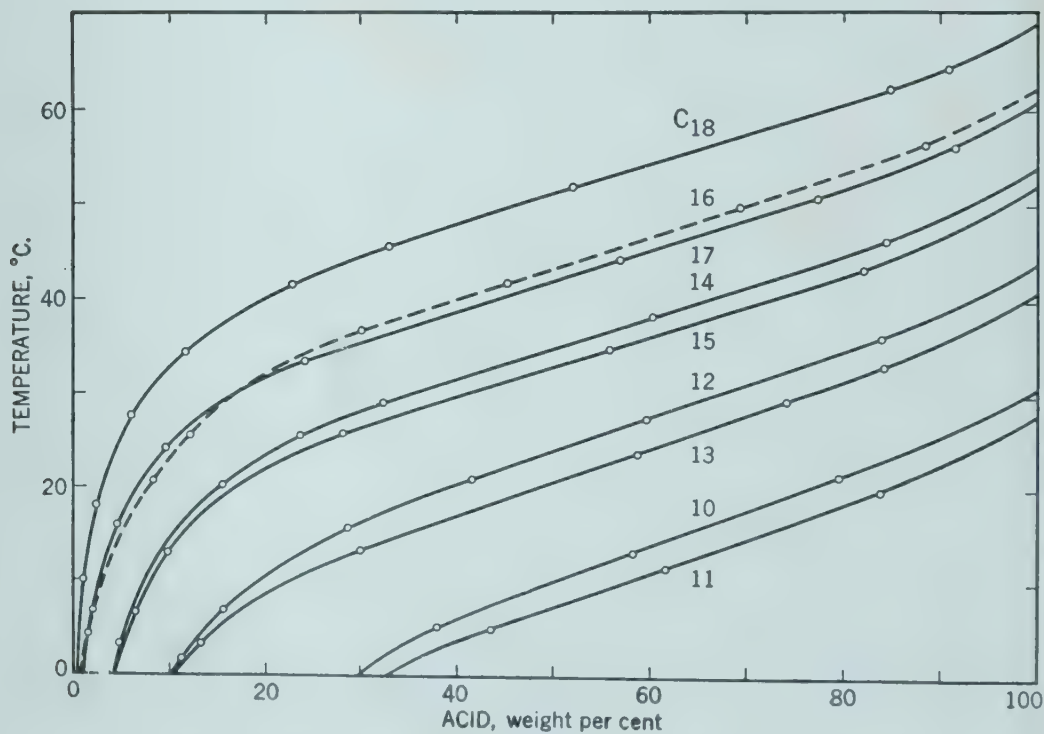


Fig. 61. Solubilities of fatty acids in 2-butanone (7).

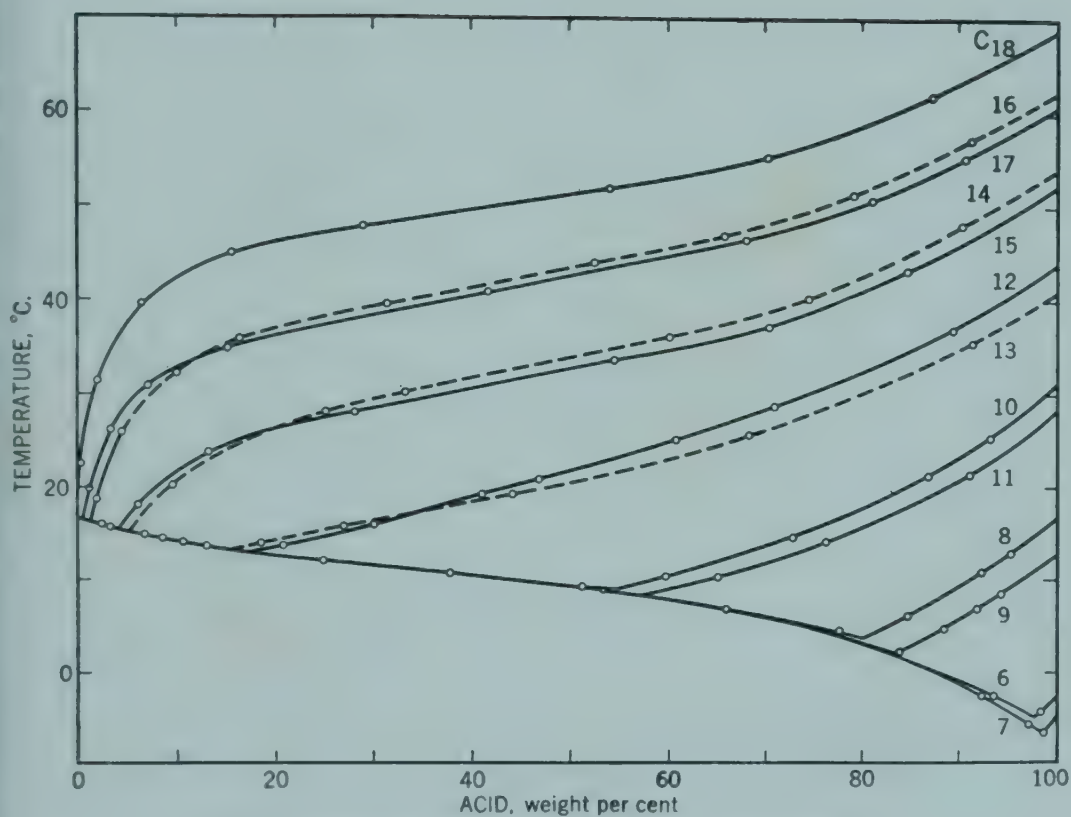


Fig. 62. Solubilities of fatty acids in glacial acetic acid (7).

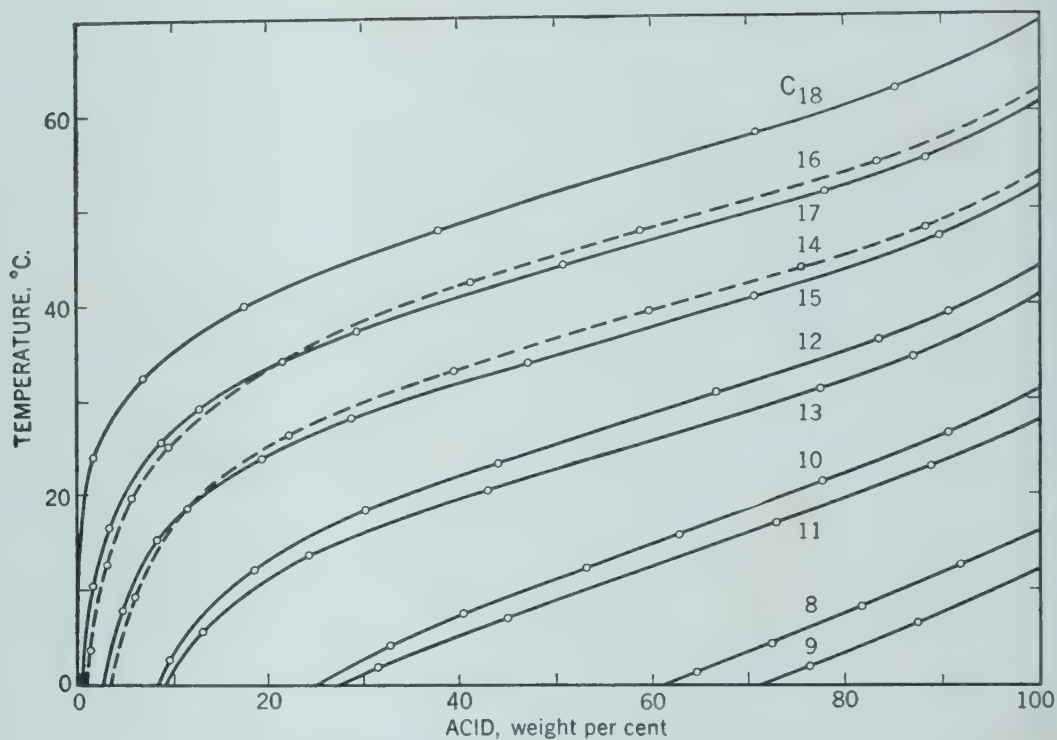


Fig. 63. Solubilities of fatty acids in ethyl acetate (49).

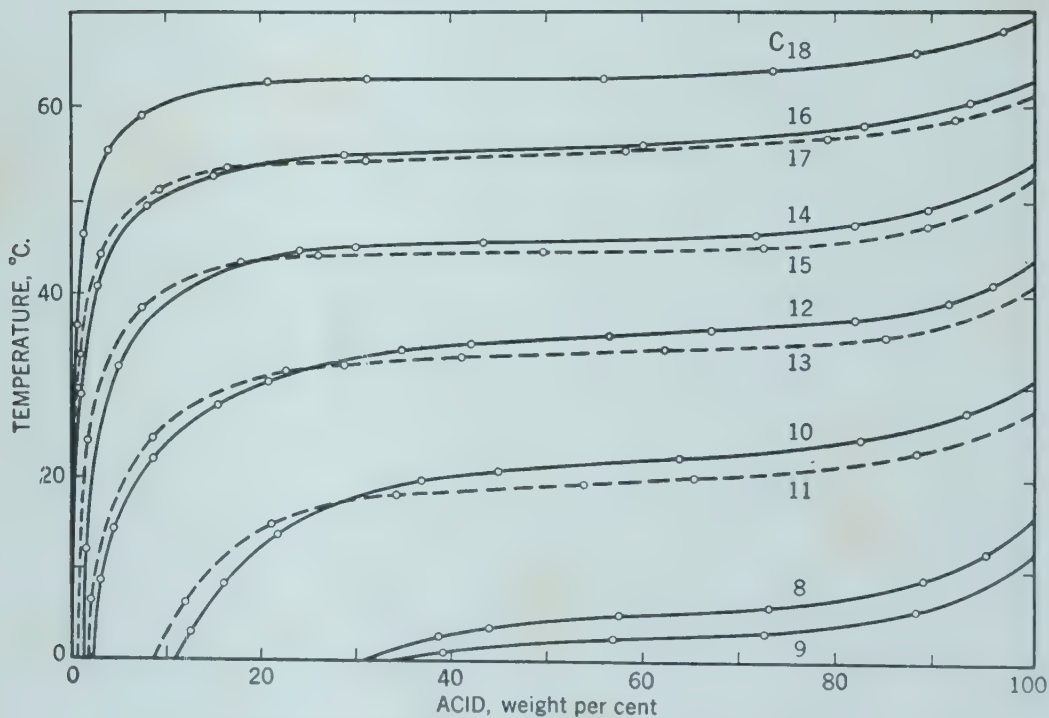


Fig. 64. Solubilities of fatty acids in acetonitrile (49).

The peculiar pairing of the solubility curves for the odd- and even-numbered acids is readily discernible by inspection of Figures 54 to 64. Without exception, the solubility curve of the even-numbered carbon acid lies above the curve of the next higher odd-numbered carbon acid throughout all, or a considerable part, of the temperature range, e.g., myristic acid is generally less soluble than pentadecanoic acid, and palmitic acid is generally less soluble than margaric (heptadecanoic) acid in the same solvent at any given temperature. The even- and odd-numbered acids, therefore, form two distinct solubility series in which the differences in spacing intervals between the curves produce the pairing observed in Figures 54 to 64.

On the basis of the solubility data assembled in Tables 162 to 176 and Figures 54 to 64, Ralston concluded that the normal saturated fatty acids are generally *more* soluble in trichloromethane and *less* soluble in nitroethane and acetonitrile than in any of the fifteen organic solvents investigated. The solubility curves for tetrachloromethane and trichloromethane, and for cyclohexane and benzene, exhibit a similar type of pairing, i.e., the next higher odd-numbered homolog is the more soluble of the pair. In the other solvents, all of which are more polar than trichloromethane, the adjacent homologs are also paired but the solubility curves intersect at moderate dilutions. Thus, the next higher odd-numbered homolog is the less soluble of each pair at temperatures below the intersection, and the solubilities of the acids decrease without alternation as the series is ascended. In the less polar solvents, this intersection of the paired solubility curves occurs above lauric acid at ordinary temperatures, while in the more polar solvents it occurs also in the lower acids.

The solubilities of the fatty acids in ethyl and butyl acetates are qualitatively similar to those observed with acetone and 2-butanone, whose polarities approximate those of the acetates. The acids are, in general, more soluble in methanol than in *n*-butanol at higher temperatures, while at lower temperatures the order is reversed. They are somewhat more soluble in the lower alcohols than in any of the other solvents investigated with the exception of trichloromethane.

Except for their solubilities in the alcohols, the normal saturated fatty acids show a marked correlation between their solubilities and the polarities of the solvents. In the nonpolar solvents, the solubilities of the acids are almost linearly dependent upon temperature, but as the polarity of the solvent increases, the relation between concentration and temperature deviates considerably from linearity.

Hoerr *et al.* (50) extended their investigations to include the solubilities of the acids from caprylic to stearic in aromatic and substituted hydrocarbon solvents including toluene, *o*-xylene, chlorobenzene, nitrobenzene, 1,4-dioxane, furfural, 1,2-dichloroethane, and nitroethane.

Compared to the extensive data now available with respect to the solubilities of the fatty acids, the information concerning the solubilities of their derivatives at moderate temperature is almost nonexistent. Ward and Singleton (51) reported data for the solubility of 1-monostearin (99.2% purity) in hexane, acetone, ethanol, isopropanol, and methanol. The method used to measure these solubilities was a modification of the synthetic method described by Andrews *et al.* (52). The results are given in Table 178.

TABLE 178
Solubility of 1-Monostearin in Various Solvents

Solvent	Temperature, °C.	Solubility, g./100 g. solvent
Acetone	8.83	0.482
	17.20	0.990
	24.08	1.957
	31.33	4.070
	41.19	9.883
Isopropanol	11.40	1.002
	18.23	1.973
	22.99	3.215
	27.25	4.953
	34.94	9.999
	43.30	24.779
	47.22	40.009
	49.01	50.000
Methanol	19.65	0.999
	25.46	2.002
	34.23	4.960
	39.49	9.809
	44.82	25.000
Ethanol	29.35	5.000
	36.72	9.960
	45.34	19.802
	45.66	29.965
	49.31	49.770
Hexane	44.28	0.227
	53.19	0.783

Some interesting observations concerning the solubilities of the various polymorphic forms of pure tristearin in several solvents at moderate temperatures have recently been reported by Hoerr and Harwood (53). They found that the solubility of tristearin was inversely proportional to the increasing polarity of the solvent. The solubilities of the α -, β' - and β -forms of tristearin in four solvents at several temperatures are given in Table 179. These data constitute virtually the only available information on the solubility of the polymorphic forms of triglycerides of the higher saturated fatty acids.

TABLE 179
Solubility of the Polymorphic Forms of Tristearin (Wt. %)^a

Solvent	α -Form				β' -Form				β -Form			
	Temperature, °C.											
	20°	30°	40°	50°	20°	30°	40°	50°	20°	30°	40°	50°
Hexane	1	9	37	81	1	1	8	35	1	1	1	12
Benzene	1	13	43	85	1	1	15	42	1	1	3	18
Carbon tetra- chloride	4	12	40	80	1	5	18	46	1	2	6	21
Chloroform	7	22	50	85	2	13	28	54	1	4	13	31

^a Calculated from plot of solubility vs. temperature.

(b) Solubility of Fatty Acids at Low Temperatures

Distillation is widely used in the laboratory and on an industrial scale to separate fatty acids and their derivatives. Other methods are also employed. The separation of fatty acids or their esters is possible by chromatographic adsorption on the basis of either the carbon chain length or the degree of unsaturation of these substances. Countercurrent distribution between two partially miscible solvents can be used to separate mixtures of fatty acids or esters. Complexing fatty acids with urea and subsequently separating the complexes on a basis of their differential solubilities is also used. Crystallization from solvents is also commonly applied in the laboratory and industrially to effect the separation of fatty materials. In order to employ the last-mentioned technique advantageously, the solution properties of fat products at low temperatures must be known.

Owing to the utility of low-temperature solvent crystallization processes for laboratory and technical preparation of fatty acids and esters, Foreman and Brown (54) investigated the solubility behavior of a num-

ber of higher fatty acids in several solvents over the temperature range $+10^{\circ}$ to -70° C. The solubility of all of the even-numbered saturated acids from C_{12} to C_{22} and three unsaturated acids, namely, oleic, linoleic, and eicosenoic, were determined in Skellysolve B, methanol, and acetone over temperature ranges shown in Figures 65 to 67.

Because of the long time required to establish equilibrium at lower temperatures, the solid and solvent were stirred for an arbitrary period of 10 hours at the selected temperature prior to determining the solubility. Solubility values obtained by approaching the selected temperature from the warm side were found to be approximately 10% higher than those obtained by approaching it from the cold side. However, in low-temperature crystallization, a solution of fatty acids is generally cooled to

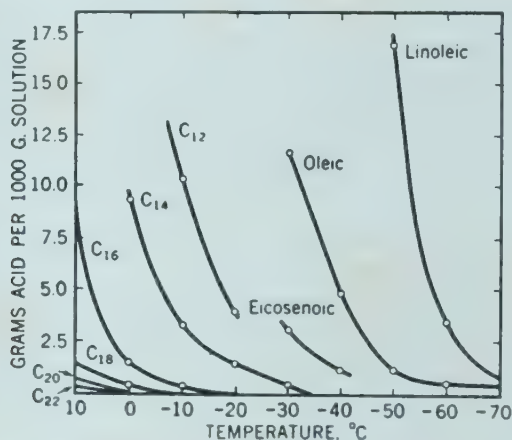


Fig. 65. Solubilities of fatty acids in Skellysolve B (54).

effect separation of a specific component; consequently the determinations were made in this manner rather than by warming to a higher temperature.

Hoerr and Harwood (55) prepared oleic and linoleic acids by a combination of crystallization and distillation methods, and determined the solubility of these acids in a variety of solvents over wide ranges of temperature and concentration. The fundamental solubility behavior of oleic and linoleic acids was found to differ but little from that of stearic acid. However, the unsaturated acids deviate to a greater extent from their respective ideal solubilities than does stearic acid. The solubility of oleic acid differs from ideal solubility to a greater extent than does linoleic acid. The data obtained by Hoerr and Harwood for the solubilities of oleic and linoleic acid are given in Table 180. They are considered to be accurate to $\pm 1\%$.

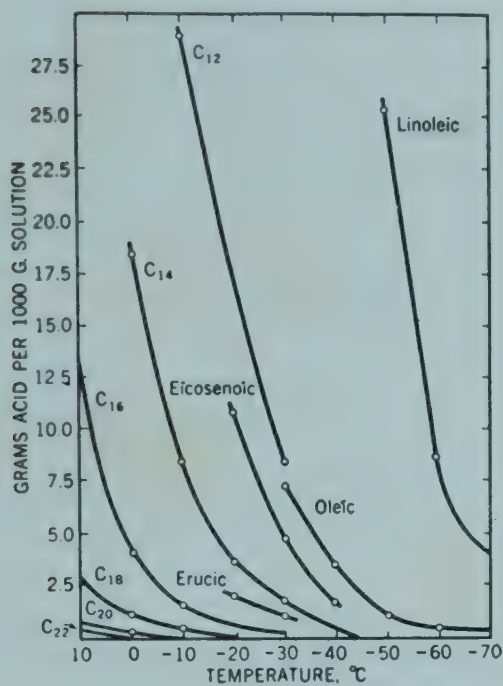


Fig. 66. Solubilities of fatty acids in methanol (54).

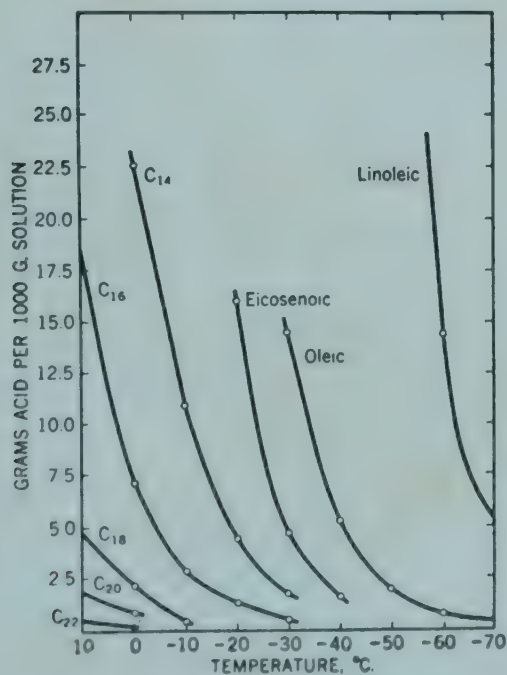


Fig. 67. Solubilities of fatty acids in acetone (54).

TABLE 180
Solubilities of Oleic and Linoleic Acids in Various Organic Solvents^a

Solvent	Solubility, g. acid per 100 g. solvent					
	-50°C.	-40°C.	-30°C.	-20°C.	-10°C.	0°C. 10°C.
<i>Oleic acid</i>						
<i>n</i> -Hexane	0.1	1.2	9.1	44.4	160	720
Benzene ^b	eutectic	eutectic			253	910
Cyclohexane ^c	eutectic	eutectic		80	233	870
Carbon tetrachloride ^d	eutectic		24.6	68	160	590
Chloroform	11.5	23.3	46.0	92	205	760
<i>o</i> -Xylene ^e	eutectic		30.5	88	250	1100
Diethyl ether	1.2	4.4	17.9	60	195	870
Acetone	0.5	1.4	5.1	27.4	159	870
2-Butanone	1.0	2.6	8.6	33.5	170	880
Methanol	0.3	0.9	4.0	31.6	250	1820
Ethanol (95%)	0.7	2.2	9.5	47.5	235	1470
2-Propanol	1.1	3.2	11.5	55.0	226	1160
<i>n</i> -Butanol	1.3	4.0	15.2	56.5	100	950
<i>Linoleic acid</i>						
<i>n</i> -Hexane	3.0	14.3	53	170	990	∞
Benzene ^f	eutectic	eutectic		320	1250	∞
Cyclohexane ^g	eutectic	eutectic		275	1210	∞
Carbon tetra- chloride ^h	eutectic		70	160	600	∞
Chloroform	19.0	40.0	88	210	770	∞
Acetone	3.3	8.6	27.2	147	1200	∞
Methanol	3.3	9.9	48.1	233	1850	∞
Ethanol (95%)	4.5	11.1	42.5	208	1150	∞
2-Propanol	6.0	11.7	45.2	203	1080	∞
<i>n</i> -Butyl	8.0	18.9	56	180	870	∞

^a C. W. Hoerr and H. J. Harwood, *J. Phys. Chem.*, **56**, 1068-1073 (1952).

^b Eutectic at 59.7 wt. % oleic acid, -9.2°.

^c Eutectic at 38.9 wt. % oleic acid, -12.1°.

^d Eutectic at 9.4 wt. % oleic acid, -25.6°.

^e Eutectic at 6.0 wt. % oleic acid, -31.0°.

^f Eutectic at 74.6 wt. % linoleic acid, -21.2°.

^g Eutectic at 51.8 wt. % linoleic acid, -28.3°.

^h Eutectic at 31.9 wt. % linoleic acid, -35.3°.

Oleic acid, a dimorphic substance, was found by Hoerr and Harwood to precipitate from its solution in benzene upon cooling in its transparent, unstable crystalline form. If the precipitated acid was held at or below its precipitation temperature, it transformed to a more opaque,

stable crystalline form which, upon heating, dissolved at temperatures above those at which precipitation occurred. This phenomenon was most evident in nonpolar and slightly polar solvents. From polar solvents only the more stable form precipitated on cooling.

Data are assembled in Table 181 for the solubilities of oleic and linoleic acids obtained by several investigators with different preparations of these acids.

TABLE 181
Comparison of Solubilities of Oleic and Linoleic Acids

	Solubility, grams acid/100 g. solvent			
Solvent	-50°C.	-40°C.	-30°C.	-20°C.
<i>Oleic</i>				
Hexane		0.1 ^c	1.2 ^c	9.05 ^c
	0.104 ^a	0.485 ^a	1.19 ^a	
		0.36 ^b	1.96 ^b	9.90 ^b
Diethyl ether		1.2 ^c	4.4 ^c	
		4.57 ^a		
Acetone		0.5 ^c	1.4 ^c	5.0 ^c
	0.189 ^a	0.519 ^a	1.444 ^a	
		0.66 ^b	2.09 ^b	5.93 ^b
Methanol		0.3 ^c	0.9 ^c	4.1 ^c
	0.098 ^a	0.330 ^a	0.713 ^a	
<i>Linoleic</i>				
Hexane	3.0 ^c			
	1.73 ^a			
Acetone	3.3 ^c			
	5.04 ^a			
Methanol	3.3 ^c			
	2.58 ^a			

^a Foreman and Brown (54).

^b Singleton (5, 73).

^c Hoerr and Harwood (55).

Hoerr and Harwood (56) also reported data for the solubilities of some saturated fatty acids and methyl esters in *n*-hexane which are assembled in Tables 182 and 183.

Kolb and Brown (57) determined the solubilities of a number of structurally different fatty acids, the results of which led them to conclude that

TABLE 182
Solubilities of *n*-Saturated Fatty Acids in *n*-Hexane (56)

Acid	Solubility, grams acid/100 g. hexane								
	-20°C.	-10°C.	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.
Caprylic	14.7	42.5	136	2600	∞				
Nonylic	25.2	74.7	249	640	∞				
Capric	2.1	6.7	23.8	81.2	290	5150	∞		
Lauric	0.2	1.5	4.9	14.7	47.7	193	1440	∞	
Myristic		0.1	1.2	4.1	11.9	41.8	198	1650	∞
Pentadecanoic			0.5	2.9	14.0	60.2	289	2950	∞
Palmitic				0.5	3.1	14.5	62.4	239	2280
Heptadecanoic				0.2	2.9	17.4	73.0	300	7602
Stearic					0.5	4.3	19.0	79.2	303

TABLE 183
Solubilities of Methyl Esters in *n*-Hexane (56)

Ester	Solubility, grams ester/100 g. hexane								
	-50° C.	-40° C.	-30° C.	-20° C.	-10° C.	0° C.	10° C.	20° C.	30° C.
Caprylate	44.3	274	∞						
Laurate	0.5	2.4	7.6	20.8	73.9	415	∞		
Myristate			0.6	3.5	14.2	53.6	238	∞	
Palmitate					2.2	14.2	55.8	229	∞
Stearate						2.2	15.9	68	286

the solubility of the acids increased with decreasing chain length and increasing degree of unsaturation. They also found that the solubility increased with distance of the point of unsaturation from the carboxyl group. Acids with *cis*-configurations were more soluble than their corresponding *trans*-isomers. Oleic acid exhibited two solubility curves in certain solvents, corresponding to its two polymorphic forms. The data of Kolb and Brown for the solubilities of thirteen acids in six organic solvents are contained in Table 184. In an investigation of the effect of the structure of the solvent on solubility, Kolb and Brown also determined the solubility of stearic, oleic, and linoleic acids in a number of normal, branched-chain and cyclic hydrocarbons, with the results given in Table 185.

TABLE 184
Solubilities of Fatty Acids^a in Various Solvents (57)

Temp., °C.	Solvent					
	Methanol	Ethyl acetate	Diethyl ether	Acetone	Toluene	Normal heptane
<i>Stearic acid</i> , $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$						
10	0.26	0.58	2.40	0.54	0.390	0.080
0	0.090	0.13	0.95	0.11	0.080	0.018
-10	0.031	0.027	0.38	0.023	0.015	0.004
-20	0.011	0.006	0.15	0.005	0.003	
-30			0.051			
<i>Oleic acid</i> , <i>cis</i> - $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$						
-20	4.02	5.95		5.20		2.25
-30	0.86	1.90		1.68	3.12	0.66
-40	0.29	0.62	5.15	0.53	0.96	0.19
-50	0.10	0.20	1.80	0.17	0.28	0.05
-60	0.03	0.057	0.61	0.055	0.075	0.011
-70			0.21			
<i>Elaidic acid</i> , <i>trans</i> - $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$						
0						0.59
-10	0.48				0.86	0.19
-20	0.18	0.29	1.40	0.26	0.20	0.06
-30	0.064	0.10	0.60	0.092	0.056	0.019
-40	0.020	0.027	0.23	0.029	0.013	0.007
-50	0.010	0.008	0.10	0.009		
<i>Linoleic acid</i> , $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$						
-50	3.10	4.40		4.10		0.98
-60	0.90	1.38		1.20		0.20
-70	0.25	0.39		0.35		0.042
<i>Arachidic acid</i> , $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$						
10	0.080	0.14	0.90	0.13	0.12	0.028
0	0.028	0.036	0.38	0.035	0.026	0.005
<i>9-Eicosenoic acid</i> , <i>cis</i> - $\text{CH}_3(\text{CH}_2)_9\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$						
-20	0.80	1.30		1.10		
-30	0.35	0.60	3.90	0.54	1.10	0.45
-40	0.15	0.26	1.70	0.27	0.30	0.15
-50	0.06	0.11	0.68	0.12	0.07	0.048
-60	0.02	0.04	0.22	0.05		0.01
<i>Petroselinic acid</i> , <i>cis</i> -6- $\text{CH}_3(\text{CH}_2)_{10}\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$						
-10						0.50
-20	0.48	0.73	3.52	0.78	0.98	0.13

(continued)

TABLE 184 (Continued)

Temp., °C.	Solvent					
	Methanol	Ethyl acetate	Diethyl ether	Acetone	Toluene	Normal heptane
-30	0.18	0.30	1.68	0.31	0.23	0.04
-40	0.06	0.11	0.76	0.11	0.046	0.009
-50	0.013	0.04	0.31	0.035	0.008	
	<i>Petroselaidic acid, trans-6-CH₃(CH₂)₁₀CH:CH(CH₂)₄COOH</i>					
0	0.50				1.40	0.22
-10	0.20	0.36		0.32	0.19	0.03
-20	0.082	0.14		0.13	0.06	0.008
-30	0.028	0.05	0.51	0.05	0.02	0.002
-40	0.01	0.018	0.19	0.019	0.008	
-50			0.07			
	<i>Stearolic acid, CH₃(CH₂)₇C:C(CH₂)₇COOH</i>					
-10	0.65	1.15	4.85	1.26	1.70	0.05
-20	0.25	0.45	2.00	0.52	0.40	0.01
-30	0.103	0.17	0.78	0.19	0.083	0.006
-40	0.04	0.065	0.32	0.07	0.018	
	<i>Palmitic acid, CH₃(CH₂)₁₄COOH</i>					
10	1.30			1.60	1.41	0.30
0	0.46	0.52	2.95	0.66	0.36	0.08
-10	0.16	0.18	1.35	0.27	0.086	0.02
-20	0.05	0.06	0.56	0.10	0.018	0.005
-30		0.018	0.21	0.038		
	<i>Behenic acid, CH₃(CH₂)₂₀COOH</i>					
10	0.019	0.055	0.48	0.05	0.04	0.012
0	0.007	0.016	0.18	0.014	0.01	0.002
-10	0.002	0.004	0.068	0.004	0.002	
	<i>Erucic acid, cis-CH₃(CH₂)₇CH:CH(CH₂)₁₁COOH</i>					
-10	0.49					0.35
-20	0.19	0.31				
-30	0.068	0.11	1.20	0.28	0.68	0.11
-40	0.024	0.04	0.49	0.10	0.16	0.03
-50	0.007		0.18	0.037	0.044	0.008
	<i>Brassicic acid, trans-CH₃(CH₂)₇CH:CH(CH₂)₁₁COOH</i>					
10	0.27	0.70		0.68	0.62	0.20
0	0.094	0.26		0.24	0.18	0.058
-10	0.035	0.096	0.78	0.065	0.05	0.016
-20	0.01	0.028	0.28	0.024	0.013	0.005
-30	0.003	0.01	0.10			

^a All values expressed in grams of acid per 100 g. solution.

TABLE 185
Solubilities of Fatty Acids^a in Various Hydrocarbon Solvents (57)

Solvent	Temperature, °C.							
	10	0	−10	−20	−40	−50	−60	−70
<i>Stearic acid</i>								
<i>n</i> -Heptane	0.080	0.018	0.004					
Methylcyclohexane	0.20	0.06	0.021	0.005				
<i>n</i> -Pentane	0.089	0.015	0.003					
Isopentane	0.096	0.040	0.017					
Diisopropyl	0.070	0.015	0.004					
Neohexane	0.04	0.01	0.003					
2-Methylpentane	0.086	0.03	0.01	0.003				
Isooctane	0.051	0.02	0.008	0.003				
<i>Oleic acid</i>								
<i>n</i> -Heptane					0.19	0.05		
Methylcyclohexane					0.34	0.11		
Diisopropyl					0.212	0.112		
Isooctane					0.162	0.070		
Neohexane					0.13	0.05		
2-Methylpentane					0.19	0.08		
<i>Linoleic acid</i>								
<i>n</i> -Heptane						0.98	0.20	0.042
Methylcyclohexane						2.06	0.38	0.072
Diisopropyl						0.94	0.17	0.032

^a All values expressed in grams acid per 100 g. solution.

TABLE 186
Solubility of Fatty Acids in Chlorinated Solvents (58)

Oleic acid		Palmitic acid		Stearic acid	
Temp., °C.	Wt., %	Temp., °C.	Wt., %	Temp., °C.	Wt., %
<i>Ethylene dichloride</i>					
9	89.60				
4.7	79.30				
-3.75	60.00				
-10.5	23.90				
-13.0	8.20				
-15.5	2.99				
-18.0	1.89				
-25.8	0.55				
<i>Carbon tetrachloride</i>					
4.8	72.68	30	16.50		
-4.3	49.77	26.3	11.90		
-9.0	35.73	14.5	3.03		
-14.5	24.26	5.5	1.0		
-19.25	13.67				
-20.0	6.42				
-21.0	3.04				
-22.5	1.51				
<i>Trichloroethylene</i>					
9.5	89.58	39	38.3	41.5	28.7
3.5	72.93	31.7	23.7	36.0	18.5
-4.5	53.39	20.0	9.4	29.3	9.9
-13.0	35.12	10.7	3.84	20.3	3.85
-21.5	19.54			12.1	1.00
-26.7	10.12				
-34.5	5.92				

The solubilities of oleic, palmitic, and stearic acids (99% purity) in several chlorinated solvents were determined by Preckshot and Nouri (58), with the results contained in Table 186. The solubilities of the acids decreased in the order trichlorethylene, carbon tetrachloride, and ethylene dichloride, except for oleic acid above -10°C . In view of the observations of Preckshot and Nouri it would seem that ethylene dichloride should be effective in separating mixtures of these acids.

Foreman and Brown (54) determined the solubility ratios of several pairs of fatty acids in various solvents which are reproduced in Table 187.

TABLE 187
Solubility Ratios^a of Fatty Acids under Various Conditions (54)

Solvent	Temp., $^{\circ}\text{C}$.	Oleic	Palmitic	Ratio:oleic/ palmitic
Methyl acetate	-25	10.0	0.74	14.7:1
Acetone	-30	14.2	0.48	30.0:1
Methanol	-30	7.08	0.20	35.4:1
Butanol	-25	62.8	1.32	47.6:1
Ethylidene dichloride	-25	26.8	3.24	82.7:1
Skellysolve B	-30	11.8	0.09	130.0:1
Carbon disulfide	-30	15.7	<0.1	>157:1
Toluene	-30	50.2	<0.1	>500:1
Ethyl ether	-40	43.7	<0.1	>450:1

Solvent	Temp., $^{\circ}\text{C}$.	Linoleic	Oleic	Ratio:linoleic/ oleic
Skellysolve B	-70	0.60	0.24	2.5:1
Carbon disulfide	-62	4.12	0.398	10.3:1
Methanol	-70	3.94	0.32	12.3:1
Acetone	-70	5.19	0.40	13.0:1

^a All solubilities expressed in g. per 1000 g. solution.

These data are especially useful in selecting conditions for separating mixtures of these acids by low-temperature fractional crystallization.

Bailey (3) plotted most of the data which appeared between 1940 and 1949 on the solubility of fatty acids in the form of graphs of log mole fraction vs. reciprocal of the absolute temperature, and with few exceptions they were found to fall on smooth curves. He observed that chloroform was the only solvent which formed ideal solutions of the higher

fatty acids over a considerable range of concentrations, as may be observed in Figure 68.

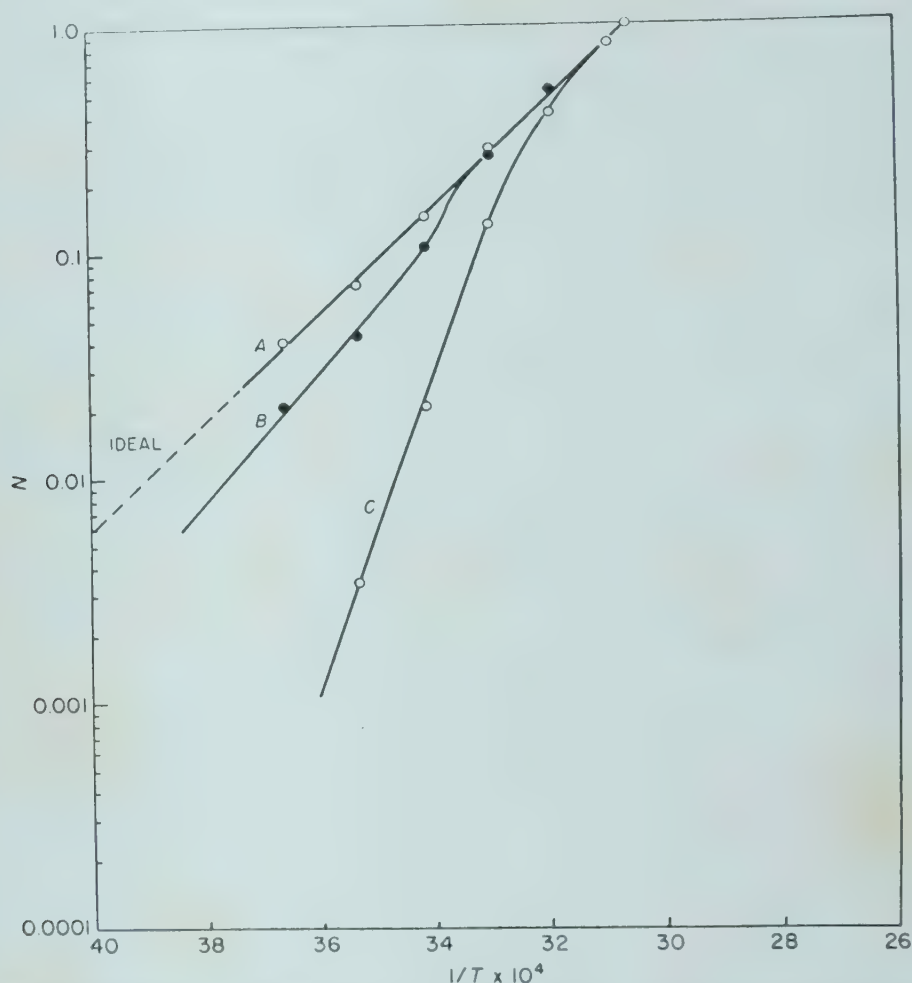


Fig. 68. Solubilities of myristic acid in (A) chloroform, (B) carbon tetrachloride, and (C) 1,2-dichloroethane (3).

(c) *Solubility of Fatty Acid Esters at Low Temperatures*

The solubility of fatty esters has been investigated by Sedgwick *et al.* (59). The property of association in solution, generally exhibited by saturated acids, does not occur with the corresponding esters. Methyl esters are somewhat more soluble on a weight basis in a given solvent than are the corresponding acids. In the series of normal alkyl esters from methyl to *n*-butyl, solubilities increase with length of the alkyl chain. Butyl stearate is twelve times more soluble in acetone at -10°C . than

methyl stearate; at 0°C. it is 3.3 times more soluble; and at 10°C., twice as soluble. Little difference was observed in the respective behaviors of methyl, ethyl, propyl, and butyl esters toward molecular association, and it was therefore assumed that the physical nature of the solutes was essentially identical. Most available evidence points to the fact that the alkyl esters of the normal aliphatic acids exist as single molecules rather than in an associated state. The solubilities of a number of normal alkyl esters of the normal aliphatic acids from C₈ to C₁₈ in methanol, ethanol and acetone are reproduced in Table 188.

TABLE 188
Solubilities^a of Esters of Fatty Acids in Some Selected Solvents (59)

Ester	-50° C.	-40° C.	-30° C.	-20° C.	-10° C.	0° C.	10° C.	20° C.	30° C.
<i>Methanol</i>									
Methyl caprylate	4.2	78	∞	∞	∞	∞	∞		
Methyl laurate			0.1	1.3	5.3	80	∞		
Methyl tridecanoate				0.3	2.9	36.5	∞		
Methyl myristate					<0.1	1.9	25		
Methyl palmitate						0.1	1.4	27	
Methyl stearate								0.6	7.2
<i>Acetone</i>									
Methyl caprylate	64	380	∞	∞	∞	∞	∞	∞	∞
Methyl laurate	0.2	0.9	3.6	12.5	67	645	∞	∞	∞
Methyl myristate			0.5	2.1	7.1	28.7	248	∞	∞
Methyl palmitate			0.1	0.4	1.3	5.2	21	250	∞
Methyl stearate					0.1	0.7	3.6	19.9	450
Ethyl stearate					0.4	1.5	5.2	40.5	1100
<i>n</i> -Propyl stearate					0.9	2.0	6.0	185	∞
<i>n</i> -Butyl stearate					1.2	2.4	6.7	345	∞
<i>95% Ethanol</i>									
Methyl caprylate	7.5	57	∞	∞	∞	∞	∞	∞	∞
Methyl laurate	<0.1	0.3	1.1	3.8	13.2	120	∞	∞	∞
Methyl tridecanoate		<0.1	0.5	2.7	11.2	70	∞	∞	∞
Methyl myristate				0.3	2.0	6.7	30.8	∞	∞
Methyl palmitate					0.2	1.1	5.0	30.4	∞
Methyl stearate						0.1	1.2	4.4	40
Ethyl stearate					0.2	0.7	2.1	6.6	180
<i>n</i> -Propyl stearate					0.6	1.5	3.4	11.5	∞
<i>n</i> -Butyl stearate					1.0	2.1	4.2	18.2	∞

^a Solubilities expressed in grams ester per 100 g. solvent.

The solubility of triglycerides has received much less attention than have the fatty acids, although one of the earliest systematic investigations

of this type by Loskit (59a) dates from 1928. The solubilities of five homotriglycerides (tricaprin to tristearin) in four solvents at various temperatures reported by Loskit are collected in Table 189. Shortly

TABLE 189
Solubility^a of Simple Saturated Triglycerides (59a)

Glyceride	Benzene		Diethyl ether		Chloroform		Ethanol	
	°C.	Sol.	°C.	Sol.	°C.	Sol.	°C.	Sol.
Tristearin	14.5	0.45	25.5	0.51	-3.4	0.46	59.8	0.074
	24.0	2.64	27.4	0.98	6.0	1.94	60.8	0.15
	26.7	5.07	31.2	2.11	11.9	4.52	62.4	0.22
	33.6	10.57	34.0	4.80	20.3	10.85	66.8	0.87
	38.1	18.91	40.3	14.25	25.8	15.71	66.9	1.55
	39.6	22.23	44.6	26.20	33.8	25.11		
	41.8	29.10	48.9	39.00	40.4	34.66		
	47.8	44.58	65.1	83.54	49.7	49.31		
	60.4	75.72			61.0	74.15		
Tripalmitin	13.7	1.74	19.0	0.75	2.5	3.08		
	18.3	4.61	24.8	2.12	8.8	7.38		
	22.8	9.69	28.0	4.49	13.5	12.13		
	26.4	16.43	31.0	8.10	18.6	18.40		
	29.5	25.30	33.8	14.06	23.3	24.24		
	34.3	37.11	37.2	21.86	28.3	31.60		
	38.4	48.07	40.3	32.62	32.3	37.67		
	48.0	56.43	43.2	42.07	41.9	52.38		
Trimyristin			47.5	58.12	52.4	71.08		
	11.3	7.56	6.7	0.57	-8.0	3.98		
	14.1	12.03	13.3	1.88	-4.7	6.12		
	15.5	14.50	18.0	4.76	0.9	10.79		
	19.1	21.94	22.2	9.54	5.5	15.04		
	21.2	27.02	25.3	15.12	10.6	21.46		
	24.9	35.85	28.0	24.46	14.8	26.36		
	30.9	49.76	31.0	34.73	19.2	32.25		
	37.2	64.69	35.7	50.53	22.6	38.04		
			40.3	65.16	24.3	40.29		
Trilaurin					38.1	62.90		
	9.0	23.50	-7.2	0.57	-12.5	13.09		
	11.6	28.25	0.8	2.25	-6.9	18.17		
	12.0	32.19	5.1	4.44	0.0	25.29		
	14.3	37.21	9.0	8.36	5.1	30.90		
	16.0	41.29	12.9	15.49	11.0	38.00		
	21.0	52.44	16.0	24.24	19.3	49.41		
	29.5	69.71	19.9	34.42	31.4	69.65		
			24.4	49.78				
			28.0	60.28				

(continued)

TABLE 189 (*Continued*)

Glyceride	Benzene		Diethyl ether		Chloroform		Ethanol	
	°C.	Sol.	°C.	Sol.	°C.	Sol.	°C.	Sol.
Tricaprin	2.2	45.29	-14.2	3.46			9.5	0.44
	7.2	56.00	-9.5	6.67			13.8	0.99
	9.4	60.39	-3.7	14.64			17.6	2.01
	11.6	64.58	-0.3	21.57			23.4	5.81
			1.2	25.36			25.1	9.87
			3.0	30.40			25.2	14.36
			4.6	36.03			58.5	29.32
			8.5	48.43				
			15.9	69.20				

^a All solubilities expressed in grams of triglyceride per 100 g. solution.

thereafter Robinson *et al.* (60) and McElroy and King (61) reported solubility data for a number of heterodiacyl glycerides, principally in ethanol.

Chen and Daubert (62) report the solubilities of heterotriacyl glycerides in four solvents. The solubilities were found to decrease in the respective solvents in the order diethyl ether, petroleum naphtha, acetone, and ethanol, as may be seen from the data in Table 190.

TABLE 190
Solubilities^a of Mixed Triacid Triglycerides at 25°C.(62)

Material	2-Acyl equals	M.p., °C.	Diethyl ether	Petro- leum ether	Acetone	Ethanol
1-Stearyl-2-acyl-3-palmitin	Myristyl	59.5	10.97	7.59	0.18	0.03
	Lauryl	57.5	16.49	9.49	0.31	0.03
	Capryl	55.0	22.87	10.60	0.59	0.03
1-Stearyl-2-acyl-3-myristin	Palmityl	58.5	11.03	5.46	0.18	0.03
	Lauryl	55.0	30.68	16.26	0.68	0.04
	Capryl	52.5	53.75	37.03	1.96	0.08
1-Stearyl-2-acyl-3-Laurin	Palmityl	52.0	72.63	58.88	1.47	0.06
	Myristyl	49.5	112.59	81.44	2.53	0.07
	Capryl	41.8	192.13	179.56	13.49	0.39
1-Stearyl-2-acyl-3-caprin	Palmityl	50.0		89.97	2.38	0.09
	Myristyl	45.0		116.35	9.03	0.31
	Lauryl	44.0		148.42	26.04	0.36

^a All solubilities expressed as grams of triglyceride per 100 g. solvent.

TABLE 191
Solubilities^a of Some Acids, Methyl Esters, Alcohols, and Triglycerides in Acetone (63)

Caproic acid	Caprylic acid	Capric acid	Lauric acid	Myristic acid	Linoleic acid	Linolenic acid
91.6 / - 31.7	138.7 / - 4.9	106.5 / 6.2	22.8 / 8.6	16.8 / 21.3	11.49 / -37.3	45.1 / -36.9
60.3 / - 38.8	84.2 / -11.2	64.2 / 0.6	9.84 / 0.6	7.51 / 13.0	5.47 / -44.4	25.8 / -41.3
38.5 / - 46.9	62.3 / -15.4	28.6 / - 7.2	6.94 / -3.5	3.27 / 5.1	2.00 / -52.1	11.4 / -49.3
24.4 / - 56.6	56.1 / -17.4	11.8 / -18.9	2.05 / -18.1	0.91 / - 9.0	0.69 / > -79.3	7.79 / -53.8
11.6 / - 70.0	59.4 / -19.3	5.55 / -29.0	0.59 / -31.4	0.53 / -12.3	0.52 / < -79.3	5.66 / -56.3
	37.2 / -22.5	2.65 / -38.7	0.20 / -42.9	0.18 / -25.3		3.22 / -62.3
	21.5 / -30.7	1.11 / -50.5		0.05 / < -79.3		2.73 / -66.9
	9.42 / -48.5	0.58 / -54.5				1.04 / > -79.3
	4.24 / -58.6					0.77 / < -79.3

Methyl caproate ^b	Methyl caprylate	Methyl caprate	Methyl laurate	Methyl myristate	Methyl palmitate	Methyl stearate
400.0 / - 76.0	330.0 / - 44.3	330.0 / - 20.0	37.2 / -13.3	32.0 / 0.5	33.0 / 12.3	5.93 / 13.0
100.0 / - 86.0	43.7 / - 58.0	96.4 / - 27.0	10.68 / -21.5	11.1 / - 6.3	10.80 / 6.5	1.10 / 1.5
42.8 / - 93.0	18.1 / - 65.5	43.4 / - 31.8				
21.2 / - 100.0	8.72 / > -79.3	25.1 / - 35.3				
5.27 / - 120.0	5.74 / < -79.3	18.1 / - 37.5				
		11.6 / - 41.8				
		5.49 / - 49.5				
		1.21 / > -79.3				
		0.21 / < -79.3				

Methyl oleate	Methyl linoleate	Methyl linolenate	Caproyl alcohol	Caprylyl alcohol	Capryl alcohol	Lauryl alcohol
208.0 / - 27.5	200.0 / - 45.7	192.0 / - 62.3	834.0 / - 49.3	14.8 / - 34.8	15.7 / - 15.2	14.7 / 0.8
98.0 / - 29.4	104.0 / - 47.5	101.0 / - 64.7	225.0 / - 52.2	9.08 / - 39.5	6.77 / - 22.3	7.43 / - 4.8

Myristyl alcohol	Palmityl alcohol	Stearyl alcohol	Oleyl alcohol	Linoleyl alcohol	Linolenyl alcohol	Tricaprylin
14.9 / - 31.0	48.4 / - 49.8	47.9 / - 68.0	66.7 / - 56.0	4.89 / - 46.8	3.12 / - 28.1	4.48 / - 9.5
27.1 / - 33.0	26.1 / - 51.7	28.2 / - 69.8	25.3 / - 59.8	1.43 / - 60.1	1.51 / - 36.1	1.54 / - 20.3
12.0 / - 35.3	11.5 / - 55.3	11.7 / - 79.0	11.6 / - 65.5	0.60 / - 68.9	0.62 / - 47.5	0.61 / - 28.2
5.42 / - 40.0	5.77 / - 59.0	6.27 / - 79.3	5.58 / - 70.7	0.43 / > - 79.3	0.21 / - 59.8	0.22 / - 37.0
0.60 / - 55.8	0.67 / - 79.3			0.12 / < - 79.3	0.05 / < - 79.3	0.08 / - 45.3
						0.04 / - 53.3
						0.01 / - 69.0

Tricaprin	Trilaurin	Trimyristin	Triolein	Trilinolein	Trilinolenin
5.41 / 1.8	5.21 / 21.5	0.43 / 24.7	185.7 / - 3.8	25.0 / - 25.0	99.8 / - 38.0
2.88 / - 1.5	2.65 / 18.0	0.11 / 18.5	64.2 / - 4.0	11.48 / - 26.0	42.7 / - 39.1
1.06 / - 8.0	1.04 / 13.8	0.06 / 16.3	25.3 / - 4.5	2.28 / - 30.7	11.5 / - 40.3
0.51 / - 13.0	0.51 / 10.3		8.32 / - 6.5	0.54 / - 37.0	5.52 / - 43.3
0.21 / - 19.5	0.23 / 6.5		1.20 / - 11.8	0.22 / - 40.7	2.11 / - 47.0
0.10 / - 21.8	0.11 / 3.3		0.52 / - 14.8	0.05 / - 47.3	1.11 / - 50.7
			0.20 / - 18.5		
			0.05 / - 25.5		

^a All values expressed as g. of solute per 100 g. of solvent at the specified temperature.^b Calculated values.

No systematic data are available for the solubilities of pure synthetic unsaturated triglycerides. Some general information has been accumulated through the industrial application of solvent fraction for the separation of natural glyceride oils.

A comprehensive investigation of the comparative solubilities in acetone of a number of fatty acids, methyl esters, triglycerides, and corresponding alcohols was reported by Privett *et al.* (63) in 1958. They applied the so-called "rising-temperature" technique in determining the solubilities that are reproduced in Table 191.

Liquid sulfur dioxide, used as a solvent for petroleum oils, has been applied in a study of the solubility and fractionation of several fatty acids and their methyl esters by Shlenk and Ener (63a). The solubility of the fatty acids was found to be much less in liquid SO_2 than in the organic solvents commonly used, whereas the methyl esters of the acids were determined to be more than one hundred times more soluble than the acids. Table 191a gives the solubilities of the fatty acids, and Table 191b the solubilities of the methyl esters.

TABLE 191a
Solubilities of Fatty Acids in SO_2 , Mg./100 g. Solvent^a

Temperature, °C.	Lauric	Myristic	Palmitic	Stearic	Linoleic	Oleic
-50					30	
-45					50	
-40					86	
-35					160	
-30						
-25	10					12
-20	22	2				27
-15	40	6				88
-10	68	12	2			270
-5	115	24	4			
0	220	44	9	3		
5		80	18	5		
10		135	40	8		
15		240	80	14		
20			130	36		
25				70		

^a The values were obtained by graphic interpolation of the experimental results.

TABLE 191b

Solubilities of Saturated Fatty Acid Methyl Esters in SO₂, g./100 g. Solvent^a (63a)

Temperature, °C.	Laurate	Myristate	Palmitate	Stearate
-50	0.6			
-45	1.25			
-40	2.6			
-35	4.5	0.25		
-30		0.6		
-25		1.25		
-20		3.2	0.15	
-15			0.40	0.05
-10			0.85	0.15
-5			2.0	0.30
0				0.65
5				1.4

^a The values were obtained by graphic interpolation of the experimental results.

These workers (63a) also determined the solubilities of various lipids in liquid SO₂, using an extraction rather than a crystallization procedure. These solubilities are given in Table 191c.

TABLE 191c

Solubilities of Various Lipids in 100g. SO₂ (°C.) (63a)

Pentadecanoic acid		10.1 mg./-9°, 16.2 mg./-5°, 53 mg./4.5°, 191 mg./14°
Elaidic acid		5.6 mg./-10.5°, 11.4 mg./-6.5°, 27 mg./-2°, 98 mg./6°, 199 mg./10°
Methyl oleate	Approx.	3.8 g./-50°
1-Monopalmitin ^a	Approx.	43 mg./-3.5°
1,3-Dipalmitin ^a	Approx.	32 mg./16.5°
Tripalmitin	Approx.	8 mg./21°
Triolein	Approx.	27 mg./-27°, 350 mg./-17°
Trilinolein	Approx.	1.25 g./-33°

^a The structure was not determined after the experiment.*(d) Anomalous Solubility and Association*

The mutual solubility effect of one acid on another is of very common occurrence and of extreme practical importance, but has received little attention. This phenomenon is responsible for the difficulty and sometimes impossibility of obtaining a pure component by crystallization of a mixture of several fatty acids, and also for the failure of small amounts

of hexabromostearic acid to separate from a large amount of tetra- and dibromostearic acid, or of small amounts of tetrabromostearic acid to separate from large amounts of dibromostearic acid. It is also responsible for the separation during crystallization of palmitic-stearic acid mixtures having the properties of margaric acid. This phenomenon is the cause of the inability to prepare absolutely pure unsaturated acids from mixtures of unsaturated acids by low-temperature crystallization.

The mutual solubility effect of one acid on another in certain solvents may be very large as was shown by Waentig and Pescheck (64), who found that the solubility of palmitic acid in carbon tetrachloride was increased 250% by the presence of lauric acid. These authors found that the mutual solubility effect decreased with increased concentration of the second component and ultimately approached a limiting concentration. An explanation of this anomalous solubility effect was sought in the hypothesis that compound formation occurred between two acids and that the compound thus formed was more soluble than the pure acid.

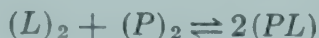
Various workers (4,64-70) have found by ebullioscopic and cryoscopic determinations of molecular weights of fatty acids in solution that these compounds are associated in certain solvents, e.g., benzene, acetic acid, cyclohexane, quinoline, pyridine, etc. Ralston and Hoerr (4) showed that, at the freezing point, the ratio of apparent to true molecular weight (M/M_0) for caprylic acid in benzene approaches a value of 2 at about 0.5 molal, indicating association in solution. In solutions of lauric acid in benzene, the value of M/M_0 approach 2 at 0.3 molal. Other investigators (65-67) have found that the values of M/M_0 for various fatty acids in benzene approach limits somewhat less than 2, and their limiting value is approached in relatively higher concentrations.

Ralston and Hoerr (4) also found from freezing point data that the values of M/M_0 for lauric acid in acetic acid approach 1.65 at about 0.2 molal.

It has already been shown, in the chapter on crystal properties, that compound formation occurs between fatty acids in the solid state. Lederer (71) found that the value of the ratio of molecular heat of evaporation of the absolute boiling point, $\lambda a/Ta$, of fatty acids at atmospheric pressure is always higher than the ratio calculated according to the Trouton-Nernst rule; he interpreted this finding as indicating that fatty acids in the liquid state are fairly completely associated while in the vapor state their density indicates they are monomolecular.

Waentig and Pescheck (64) postulated the occurrence of three such com-

pounds in a solution of two fatty acids which are capable of associating in a given solvent in accordance with the following equation:



and which presupposes that each of the compounds would exert a mutual solubility effect. On this assumption, a mutual solubility effect should not be observed in solvents in which association of the acids does not occur, and they claimed this to be the case. They observed mutual solubility effects with solvents such as carbon tetrachloride, chloroform, benzene, toluene, and nitrobenzene, in which the fatty acids are dimolecularly associated, but not with ethanol, diethyl ether, ethyl acetate, and benzaldehyde, in which the fatty acids are monomolecular.

These authors further concluded that the mutual solubility effect is independent of temperature but that it is markedly affected by even traces of moisture. It has also been emphasized by Waentig and Pescheck that a determination of the temperature at which a definite amount of fatty acid just dissolves in a definite amount of solvent affords an extraordinarily precise determination of the purity of the fatty acid—more so than the determination of the melting point.

Ralston and Hoerr (72) disagreed with the explanation offered by Waentig and Pescheck for the mutual solubility influence of one fatty acid on another. According to the former authors, the determination of the degree of association of the higher aliphatic compounds by cryoscopic and ebullioscopic measurements, upon which Waentig and Pescheck based their conclusions, tends to yield erroneous results, and the modern concept of hydrogen bonding indicates that the fatty acids (at least the lower homologs) exist as double molecules in all states, even in solution.

Ralston and Hoerr (72) determined the solubility of various binary mixtures of palmitic and stearic acids in benzene, acetone, chloroform, and ethyl acetate. They also determined the solubility of various mixtures of palmitic acid and heptadecane in 2-butanone. In the case of the palmitic–stearic acid mixture the greatest solubility was found to correspond to the 70:30 palmitic–stearic acid eutectic rather than to the 50:50 compound. As a matter of fact, the most soluble mixture was found to correspond to the minimum melting point composition of the palmitic–stearic acid system. The temperature–solubility curves of Ralston and Hoerr indicate that the chief factor which apparently governs the solubility of a given mixture is the melting point rather than the proportion of bimolecular complex present in the mixture. This observation is considered to be thermodynamically sound, since solubility is a function of

the latent heat of fusion of a solute according to interpretation of Raoult's law. Furthermore, the solubility relationships observed by Ralston and Hoerr were not appreciably altered by change of solvent; benzene (non-polar), chloroform (slightly polar), ethyl acetate (moderately polar), and acetone (highly polar) gave temperature-solubility curves that exhibited remarkable uniformity.

Rao and Rao (72a) determined the mutual solubility and equilibrium distribution data at 31°C. for the ternary liquid systems water-propionic acid-solvent. Solubility was determined by the turbidity method. In all of the systems studied, propionic acid was distributed in favor of the aqueous phase, in increasing amounts in the solvent order benzene, toluene, cyclohexene, cyclohexane, and hexane. Typical of the mutual solubility data reported by these authors are the results given in Table 191d.

TABLE 191d
Mutual Solubility (Wt. %) for the System Propionic
Acid-Water-Hexane at 31°C (72a)

Propionic acid	Water	Hexane
22.1	77.6	0.3
32.5	67.0	0.5
40.8	58.6	0.6
44.5	54.8	0.7
50.0	49.0	1.0
53.7	45.1	1.2
57.9	40.1	2.1
60.4	36.9	2.7
69.0	27.3	3.7
74.3	21.0	4.7
74.7	19.0	6.3
74.8	17.4	7.8
74.7	15.1	10.2
74.4	13.5	12.1
73.5	11.9	14.6
72.0	10.5	17.5
70.2	9.2	20.6
67.1	7.4	25.5
63.9	6.4	29.7
60.1	4.7	35.2
54.5	3.2	42.3
48.3	1.9	49.8
43.0	1.2	55.8

Solubility of Binary Mixtures of Fatty Acids. The resolution of mixtures of fatty acids by fractionation from solvents is fundamentally important in the laboratory preparation of pure acids, and is also of considerable industrial importance. Despite this importance, relatively few systematic investigations of the phase relations of such solutions have been made.

The only reported investigations relating to the composition of the solid and liquid phases existing in equilibrium in ternary systems composed of two fatty acids and a solvent are those of Singleton (5,73). The systems investigated by this author are oleic–stearic–acetone, oleic–stearic–hexane, oleic–palmitic–acetone, and oleic–palmitic hexane, at 0, –10, –20, –30, and –40°. The phase diagrams of these systems at the indicated temperatures show that the intersolubilizing effect of oleic acid on either palmitic or stearic acid is greater in commercial hexane than in acetone, and also that oleic acid of high purity can be obtained from a mixture of this acid with stearic or palmitic acid by selecting the proper conditions of crystallization.

A typical phase diagram of oleic–stearic–hexane is reproduced in Figure 69, which represents the compositions of the liquid and solid phases in

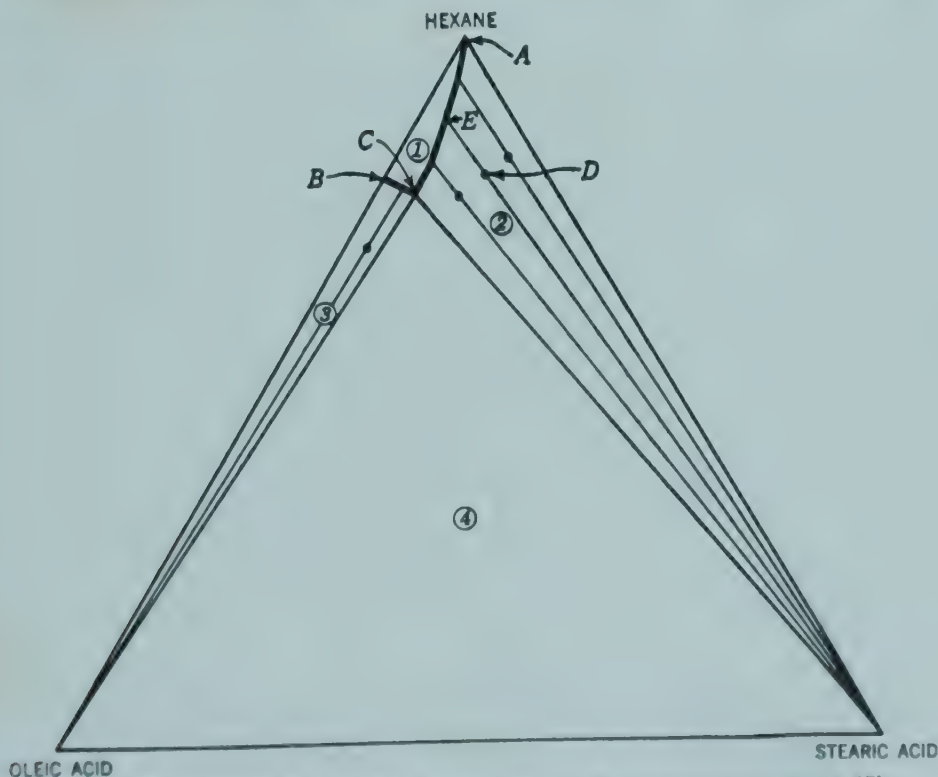


Fig. 69. Solubilities of oleic and stearic acids in commercial hexane (5).

equilibrium when varying proportions of oleic and stearic acids in commercial hexane are cooled to -20° . The point *A* represents the solubility of stearic acid (0.0005%) in commercial hexane; *B* represents that of oleic acid (8.999%), and *C* represents the composition of a solution in equilibrium with *both* stearic and oleic acids. This solution contains approximately 0.12% stearic acid. Area 1 represents a single-phase solution. Any mixture whose composition falls in area 2, such as *D*, will at -20°C . yield stearic acid and a solution whose composition is indicated by the interaction of the tie line, *DE*, with the boundary of the single-phase area. A mixture in the area 3 will yield oleic acid and a solution of composition between *B* and *C* determined by the intersection of a tie line from the oleic acid apex with the boundary of area 1. In area 4, mixtures separate into two solid phases, stearic acid and oleic acid, and a solution of fixed composition *C*.

Solubility of Fatty Acids in Liquid Propane. The hydrocarbon, propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, boils at -42.4°C . but can be liquefied at ordinary temperatures and can, therefore, serve as a solvent for fatty acids similarly to the higher boiling hydrocarbons. The specific gravity of liquid propane in the region of its boiling point is 0.5824 or somewhat lower than *n*-hexane, 0.6594²⁰, which is widely used as a solvent for fats and fatty acids.

The availability of propane in large quantities has led to its application in solvent refining (dewaxing) of lubricating oils and has attracted the attention of various workers as a possible medium for solvent refining of vegetable oils and for the fractionation of fatty acids.

Hixson and co-workers (74-76) investigated the various binary and ternary systems composed of liquid propane and fatty acids, monoesters, triglycerides, and vegetable oils. These systems included: propane-oleic acid (74); propane-refined cottonseed oil, propane-oleic acid-refined cottonseed oil, propane-tristearin, propane-tripalmitin, propane-tricaprylin (75); propane-stearic acid, propane-oleic acid, propane-cetyl stearate, and propane-stearic acid-palmitic acid (76).

Bogash and Hixson (77) determined the critical solution temperatures in propane of stearic and palmitic acids, and trimyristin and trilaurin. The addition of methane lowers these solution temperatures. These data might be effective in the separation of long-chain fatty acids or their triglycerides.

The binary systems of liquid propane and fatty acids and esters investigated by Drew and Hixson (76) exhibited typical U-shaped phase diagrams having critical solution temperatures as follows: oleic acid, 91.1° ;

stearic acid, 91.4°; palmitic acid, 96.9°; cetyl stearate, 95.2°; tristearin, 69.2°; tripalmitin, 73.5°; and tricaprylin, 100.5°C. A plot of the critical solution temperatures against effective molecular weight indicated that the free acids were associated in bimolecular form.

The solubility curves for the binary saturated acid and binary mono-ester systems with liquid propane indicated complete miscibility in all proportions from the melting point of the acid or ester up to the critical solution temperature, which is near the critical temperature of propane. The solubility data for the propane-palmitic acid-stearic acid system show that separation of these two acids in liquid propane is impractical.

(e) Solubilities of Other Long-Chain Compounds

In addition to the organic solvent-fatty acid systems previously discussed, Ralston and co-workers investigated a number of other related systems, including the higher aliphatic hydrocarbons (78), symmetrical ketones (79), primary alcohols (80), primary amines (81), amine hydrochlorides and acetates (82), secondary amines (83), tertiary amines (84), nitriles (85), amides (86), anilides (86), and *N,N*-diphenylamides (86).

Seidell (6) brought together, in his solubility tables, data with reference to other fatty acid systems whose discussion has been omitted here. The most extensive series of these systems have ethanol as the solvent and a fatty acid (behenic, lignoceric, oleic, elaidic, erucic, and eleostearic) or fatty acid ester (cetyl palmitate, cetyl stearate, dicaprin, dilaurin, dimyristin, dipalmitin, tricaprylin, tricaprin, trilaurin, trimyristin, tripalmitin, and tristearin) as solute. However, many of the systems, especially those with reference to the fatty acid esters, are comprised of solvents other than alcohol, principally petroleum ether, benzene, diethyl ether, chloroform, and carbon disulfide. The solubility of hexabromostearic acid has been reported for twenty-eight different solvents.

The solubilities of lead salts of several branched-chain fatty acids in diethyl ether and in ethanol at 20–25°C. have been reported by Cason and Sumrell (87). The lead salts of most of these branched-chain acids, are very soluble in diethyl ether and much less so in ethanol, as may be seen by inspection of the data in Table 192.

TABLE 192
Solubilities^a of the Lead Salts of Branched-Chain Fatty Acids (87)

Acid	Solubility	
	Diethyl ether	Ethanol
Hendecanoic	0.004	0.018
2- <i>n</i> -Butyl-2-ethylnonanoic	>36	>36
4-Methyloctadecanoic	>15	0.09
8-Methyloctadecanoic	>17	0.34
11-Methyloctadecanoic	>25	0.30
14-Methyloctadecanoic	0.40	0.02
16-Methyloctadecanoic	0.10	
15-Ethylheptadecanoic	>28	0.12
3,3-Dimethyloctadecanoic	>19	0.20
12- <i>n</i> -Hexyloctadecanoic	>20	0.16
6-Methyltetracosanoic	0.34	0.04
10-Methyltetracosanoic	>22	0.09

^a All solubilities expressed as g. of lead salt per 100 ml. of solvent.

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